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Flame Retardants for Plastics and Textiles

Practical Applications

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Preface

For several years, the authors have taught a short course on flame retardancy under the auspices of the Business Communications Corp. This course has been found useful by persons entering the field of flame retardancy or who were facing particular problems of flame retarding plastics. One of us (S.V.L.) presented an introductory lecture discussing mode of action of main classes of flame retardants and one of us (E.D.W.) presented a survey of flame retardants in commercial use or advanced development, discussed polymer class by polymer class. The present volume is a much-extended coverage of flame retardants from the same practical point of view. It is intended to be of use especially by plastics compounders, textile technologists and by R&D workers in this field. Our coverage is mainly chemistry-oriented and formulation-oriented.

We have not included flame retardant coatings, "firestops" and fire-barrier materials, flame retardants for wood or paper, and inherently flame resistant polymers.

We have made an effort to reference much of the information presented, but in the many cases where references are not cited, it can be assumed that the source is supplier's literature, supplemented by discussions with suppliers where needed.

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1 Introduction¹⁾

The term “flame retardants” should be clearly understood to mean materials (additive or reactive) which deter or extinguish flame propagation under standard laboratory test conditions. The definition set forth by the relevant ASTM terminology subcommittee for a flame retardant chemical is “a chemical which, when added to a combustible material, delays ignition and reduced flame spread of the resulting material when exposed to flame impingement” [1]. Note the relative rather than absolute language. Note also that terms such as “fireproof” or “flameproof” can be misleading and should not be used. It is also important for everyone working in this field as well as users of flame retardants to understand that tests run under standard small scale conditions do not necessarily predict the behavior of the materials under real fire conditions. Substantially all flame retardants can be defeated in a large fire. In the present volume, the use of terms such as “flame retardant” should in no way be construed as warranting or suggesting adequate performance in a real fire.

Another important consideration is that flammability tests run on small standard sized samples may not properly represent the performance of the final product containing the formulated plastic. Configuration, wall thickness, orientation, coatings and adjacent materials can greatly affect flame retardant performance. The manufacturer should test the final product under use (and abuse) conditions. The relatively new European single-burning item test is a step in this direction. In the U.S., the Underwriters Laboratory has long recognized the importance of realistic testing. However, many tests called for in codes and purchase specifications still fall short of representing real fire conditions. Some of these methods, like the time-honored E-84 “Steiner 25-ft. tunnel,” and automotive MVSS 302 are considered by many fire experts to be in severe need of upgrading or replacing, even though they are cited in many codes and specifications.

Despite not giving absolute protection against fire, flame retardants have played, and continue to play, an important role in reducing the occurrence and severity of fire. One dramatic demonstration was the order-of-magnitude greater number of fires, with many fatalities, involving European television sets which were non-flame-retarded compared to the U.S. where television sets had to meet the UL 94 V0 standard [2, 3]. A broad assessment of the need for flame retardants was published by Prof. Nelson [4].

Flame retardants also represent a commercially important family of plastics additives and textile treatments, with an over \$4 billion sales estimated for 2008. Flame retardants are one of the fastest growing plastics additive classes worldwide [5].

1) It has been our intention to cite tradenames and trademarks correctly, and to distinguish them from common or generic names. However, the use of general descriptive names, trademarks, etc. in this publication, even if the former are not especially identified, is not to be construed as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

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Some suggested sources (books, journals, Web sites, conferences) for further flame retardancy information can be found in the Appendix 1. Sources (mostly U.S.) for the flame retardant chemicals are in Appendix 2.

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2 Flame Retardants in Commercial Use or Development for Polyolefins

2.1 Introduction

In this chapter, the authors concentrate on presently used and developing technology for flame retarding polyolefins, including those copolymers that have properties mainly reflecting their aliphatic hydrocarbon components. Polyolefin polymers that will be discussed in this chapter include the principle homopolymers, such as polyethylene, polypropylene, and polybutenes, copolymers with other olefins, copolymers with vinyl monomers such as vinyl acetate, and the ethylene-propylene rubbers. The diene elastomers and natural rubber are briefly discussed. Copolymers with styrene and block copolymers with styrene are discussed in Chapter 3. An earlier review (2002) on flame retardancy of polyolefins is by Albemarle authors [1].

Theory and mechanism of thermal decomposition and stabilization are outside the scope of the present review, although we will briefly allude to the usually accepted mode of action explanation for most of the flame retardants. The reader is referred to our recent review [2] and several chapters in the book edited by Grand and Wilkie [3]. An earlier book, still useful on basic chemistry of flame retardants, is Cullis and Hirschler [4].

The use of adequate mixing equipment and methodology are important to achieve dispersion of the usually-solid powder additives. Higher filler levels, or finely divided materials which tend to reaggregate, or those additives which have their thermal stabilities only slightly above processing temperatures, are particularly challenging. A brief discussion of these problems, and the applicability of different kinds of equipment has been published [5]. In general, good dispersion of the flame retardants and synergists is important. It is often found advantageous to add the solid flame retardant prior to the addition of plasticizing or processing aid additives.

This book contains short discussion of test methods and standards but for a more complete overview the reader is referred to an updated compendium by Troitzsch [6]. European Union standards and test methods are in a state of transition, with both new EU standards and some old national standards in use; recent overview papers should be consulted, for example, by Wickström [7]. A useful criteria of a popular small scale laboratory test, oxygen index (limiting oxygen index, LOI), often used to characterize flammability, shows poor or mediocre correlation of this measurement to cone calorimetric measurements and other burn tests [8]. However, small scale tests such as LOI and UL-94 can be useful, to supplement cone data [9]. Because of the complexity of the topic, we find it necessary to organize it by chemistry and then again by application, which will lead to some duplication.

2.2 Generalizations

Primarily aliphatic polymers have high heats of combustion approximating to typical hydrocarbon fuels. For example, gross heats of combustion in kJ/g are: polyethylene 47.74; polypropylene 45.80. The hydrocarbon polymers also tend to burn with low char yields if not compounded with char-forming additives. There is a very rough relationship of thermodynamic heat of combustion for low-char-forming materials to flammability as measured by, for example, oxygen index [10]. Polypropylene poses further difficulties in flame retardancy because of its high crystallinity. High loadings of flame retardants in polypropylene increase brittleness and impair mechanical performance. On the other hand, less crystalline or rubbery copolymers such as EPR, EPDM, other olefin copolymers and diene elastomers generally accept high loadings of flame retardant additives while retaining useful properties. Good dispersion of solid additives is favored by keeping the temperature as low as possible to build viscosity and shear.

In the broadest sense, efforts to flame retard this category of polymer have relied on endothermic additives, flame-quenching (kinetic) inhibitors, barrier-forming materials, and sometimes combinations of these approaches.

2.3 Endothermic Additives (Mainly Metal Hydroxides)

These have, as a general characteristic, rather low prices compared to other categories of flame retardants, and have a requirement for relatively high loadings. They also tend to inspire less controversy regarding environmental aspects. They generally have low toxicities, even to the point where they can be ingested without harm. They are often viewed as “minerals” not “chemicals.”

2.3.1 Alumina Trihydrate (Aluminum Trihydroxide, ATH; Mineral Name: Bauxite)

ATH is, by weight and for all applications, the largest flame retardant at this time, although it is exceeded on a monetary basis by tetrabromobisphenol A and decabromodiphenyl oxide. There are two main categories, ground and precipitated. Both varieties have rather similar thermal properties, but differ in their particle size and shape. Both have their origin in the ore, bauxite, which is almost always processed by the Bayer Process. Bauxite is dissolved in strong caustic, filtered to remove iron and silica minerals and other contaminants, then the solution is cooled and the aluminum trihydroxide allowed to crystallize out. The product is controlled by seeding or selective nucleation, precipitation temperature and cooling rate. Its size is generally above 50 μm . It is commercially wet- or dry-ground to produce median size ranges of “ground Bayer hydrate” from about 1.5 μm to about 35 μm , and varying in color from almost white to beige. The main impurities, which depend on the ore source, are iron compounds, silicates, soda and some organic materials.

To make purer, whiter, ATH, the Bayer hydrate may be redissolved in caustic and reprecipitated. The precipitated ATH usually has a median size range between 0.25 and 3.0 μm , lower

iron, silica, soluble soda and organic content, and lower surface areas than comparable sized ground ATH.

A small percentage of commercial ATH is surface treated (see further discussion below).

2.3.2 Properties of ATH

ATH is a white or off-white powder, with a specific gravity of 2.42 and a hardness (Mohs scale) of 3.0, compared to anhydrous alumina (corundum) which has a hardness of 9. The formula of ATH is more correctly expressed as $\text{Al}(\text{OH})_3$, not the misleading hydrate formula $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. ATH loses 34.6 % of its weight by 350 °C, but begins losing weight at slightly above 200 °C and by 300 °C it is essentially anhydrous alumina. Careful control of time and temperature can produce alumina monohydrate or boehmite, $\text{AlO}(\text{OH})$, sometimes expressed as $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and this has been proposed as flame retardant for polymers processed at high temperatures. ATH and its dehydration products are generally considered non-toxic and not an environmental problem.

ATH is available in a wide range of particle sizes. Larger particles are usually preferred for “solid surface” products, *i. e.*, cast stone made with a methacrylic or unsaturated polyester matrix. For these products, the aesthetic and hardness contribution of the ATH is usually the main consideration; flame retardancy is an incidental bonus.

Viscosity considerations are important both in thermoset systems such as polyester resins and in thermoplastic processing. Generally, the finer the particle size, the higher the viscosity at a given loading. Bimodal combinations have been shown to allow higher loadings at tractable viscosity; evidence from studies done at Huber in thermoset resins probably is applicable to thermoplastics [11].

2.3.3 ATH Modifications

Surface treated ATH is commercially available with treatments such as stearic acid. These tend to be better flowing and are more rapidly miscible into polymer melts. However, mechanical, electrical and even flame retardant properties are often not improved or even somewhat compromised.

Aminosilane surface treatment of ATH can improve the physical properties of an olefin polymer or copolymer. A comparison has been published by Albemarle [12] showing that in EVA, an aminosilane coated ATH substantially increased tensile strength, almost doubled elongation at break, slightly increased melt flow, and greatly increased volume resistivity (tested after 28 days in water at 50 °C) by four orders of magnitude. Surface treatment of ATH by combinations of functional silanes applied together with fatty acid derivatives are also claimed [13]. Flame retardancy is normally improved somewhat by silanation but the main benefit is mechanical and electrical properties.

As an alternative to surface treatment, control of precipitation conditions can provide improved versions of ATH. For instance, Nabaltec's Apyral® 40 CD has low oil absorption, low dust, good conveyance properties, good wetting and dispersion in polyolefins [14]. It permits compounding output to be increased as much as 20–30 %. Melt flow rate is

substantially improved. An even lower viscosity grade, Apyral 20 X, is available but this would appear to have larger particles; it permits high loadings (thus high flame retardancy) and can be used where settling, filtration on glass fiber mats, and surface finish are not so crucial.

2.3.4 Synergists and Adjuvants with ATH

Flame retardancy benefits have been found by addition of small amounts of catalytic metals, notably nickel, to ATH; for example, a nickel-oxide-modified ATH can give a V-0 rating in PP at 47.6 % whereas without the nickel, 55 % was needed. Japanese producers have offered such products [15]; color and toxicity problems have probably deterred their use.

Enhancement of the flame retardant action of ATH with zinc borates has been established. In EVA, improved char (and inorganic barrier) formation is noted. Replacing 65 % ATH by 60 % ATH plus 5 % Rio Tinto's Firebrake® ZB lowers the peak rate of heat release in the cone calorimeter, and causes a major depression of the second (burn-off) peak of heat release [16]. Studies at Nabaltec [14] have confirmed the zinc borate enhancement of the action of ATH in EVA and polyolefins. Evidence has also been published for the beneficial (perhaps synergistic) action of alumina monohydrate (boehmite) added in the range of 5 % to ATH in the range of 65 %. The zinc borates are also recommended for use in EPDM, particularly in combination with ATH, MDH or a clay. In formulations of elastomers with high loadings of carbon black, especially those with high surface area, afterglow may be noted and can be controlled by adding zinc (or barium) borates.

2.3.5 Magnesium Hydroxide (Magnesium Dihydroxide, MDH)

At present, MDH is used at a much lower volume than ATH, however, in some applications it competes; in applications above the water-loss range of ATH (*i. e.*, around 200 °C) it can be used where ATH cannot. There are several types [17, 18]. The higher-priced varieties of MDH are Kisuma® with ordered uniform crystals from Kyowa (Japan) which are made from MgCl_2 and lime with precisely controlled crystallization, and most or all grades are surface-treated. There is a less costly Magnifin® (Albemarle) made from magnesium silicate ore via MgCl_2 and MgO . In Israel, the Aman process converts MgCl_2 brine by hydrolysis to MgO , which is then hydrated to MDH. A still lower-cost less-ordered MagShield® (Martin Marietta) is made from MgCl_2 brine and lime or dolomitic lime. They are not interchangeable. Polymer melt shearing and property degradation can occur, for example in EVA or PP with inappropriate choice. Mechanical properties, flame retardancy and water resistance can all vary with the type of MDH used. Typical levels to achieve a V-0 rating in a polyolefin are in the 65 % vicinity.

A new Martin Marietta product is partially coated to get good flow properties, but allowing the user to add more surface treatment in compounding for specific applications. MDH is growing rapidly with main applications primary in insulation, jacket insulation, electrical connectors, cable boxes, office divider frames, and automobile sound-deadening panels.

Surface-treated magnesium hydroxide is available, a typical treatment being with stearic acid which aids processing, however, it can increase color in the filled plastic [19]. Alternative to

the use of stearic acid, treatment of MDH with a vinyl- and alkylsilane can also improve flame retardancy. A detailed study of these alternatives, including a discussion of the criticality of the amount of surface treatment applied and effects of the manner of its application has been published by Huber [20]. It is shown that use of a pretreated additive can insure better processing and compound properties than the *in-situ* treatment during compounding. It is also shown that a functionalized PE (presumably a maleic grafted PE) as a compatibilizing agent can further improve fire performance.

A proprietary treatment was developed at J.M. Huber to make Vertex® 100, a coarser particle size but higher surface area MDH, which shows improved processing, mechanical properties and color. A patent suggest that the system may make use of a reactive silane oligomer [21]. A study by Chen [22] shows a comparison in EPDM of MDH treated with monomeric vinylsilane or oligomeric vinylsilane of low and medium vinyl content. Such surface treatment can enhance processing (lower viscosity), color and electrical properties, as well as providing better flame retardancy properties than untreated or stearic-acid-treated MDH. There is an optimum level of silane treatment; excessive amounts can be detrimental to performance.

MDH coating optimization has been conducted by wire and cable researchers to obtain a high level of processability, fire performance, and strength [23]. Earlier patents to the Scapa group indicate the use of trialkoxysilanes to treat MDH [24]. Combinations of functional polysiloxanes and fatty acid derivatives are also used to treat MDH with improvement of physical properties of the polymer compositions [13].

In the above-referenced study in polyolefins by Chen [22], it was shown that the particle size distribution of MDH as well as the surface treatment has a substantial impact on the compound properties. An MDH of narrow particle size distribution, average particle size 0.8 microns and enhanced surface area of 13 m²/g, gave an improved balance of material toughness, modulus, tensile and fire properties.

2.3.6 Synergism of MDH with Zinc Borate

The flame retardant performance of MDH can be synergized by zinc borate (Rio Tinto's Firebrake® ZB or Marshall Additive Technologies CT ZB800). In general, zinc borate is useful as a synergist with MDH at about a 1 : 10 to 1 : 5 weight ratio. At 5 : 1 ratio of MDH (best results with Huber Vertex® 100), a total loading of 64 % gives a V-0 rating and LOI of 39 in EVA. This slightly lower loading permits the use of a higher molecular weight EVA with adequate processing rheology [25].

2.3.7 Other Synergistic MDH Combinations

In some studies, a moderate synergism has been found between ATH and MDH in polyolefins [26, 27]. However, other workers [18] find additivity but no synergism. They do show a non-linear (diminishing effect) relation when MDH is added to ATH. Synergism "an effect greater than additive", in apparently positive cases, may result from non-linear flame retardancy vs. concentration relations and the inappropriate application of a linear additivity model [28, 29]. Some further augmentation of flame retardancy can be obtained by also adding a silicone, a melamine phosphate or a nanoclay to an MDH formulation [16].

MDH was enhanced in regard to flame retardant effect in EVA by porous silica or talc which enhanced the mass transfer barrier and char forming action. Even more intense was the further enhancement by potassium carbonate treated with magnesium stearate [30].

2.3.8 Ultracarb® (Huntite-Hydromagnesite Mixture)

This is a natural mineral mined in Greece and Turkey and sold by Minelco. It is an approximately equal mixture of huntite, $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ and hydromagnesite, $\text{Mg}_4(\text{CO}_3)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, which is dried, crushed, finely ground and classified to produce a white powder, Ultracarb® U5, the majority of its particles having less than 1 micron size. It gives off both water and carbon dioxide when heated, with a minor loss at about 230 °C (thus, somewhat more thermally stable than ATH), and major losses at about 420 and 550 °C, the total endotherm being about 1000 J/g and the total weight loss being about 53 %. It provides approximately the same physical properties to a polyolefin as does ATH, and may have a cost advantage.

A number of surface treated varieties are also available which besides easier dispersion in polyolefins also show better mechanical, electrical and flammability properties.

2.3.9 Talc

Talc is a natural magnesium silicate with major usage (probably over 500 000 tons/yr.) compounded into polymers for reinforcement, stiffness, dimensional stability, low shrinkage and improved processability. It has a lamellar character and tends to form a barrier to mass transfer in a burning polymer. In an EVA or PP, talc such as 10M2 grade can substitute up to 15 % of the hydrated filler (ATH or MDH) with at least as good flame retardancy and often improved mechanical properties [31].

Clays are discussed below under flame retardants for elastomers, where high filler loadings can be tolerated.

2.4 Halogenated Flame Retardants

This category actually covers bromine and chlorine-containing flame retardants. Iodine would probably work but is too expensive and its compounds tend to be relatively unstable with respect to heat and especially to light.

Fluorine plays a useful role in flame retardancy, particularly in the form of stable essentially non-combustible fluoropolymers, such as Teflon®, a substantially non-combustible thermoplastic and FEP — a fluorine containing elastomer used prominently in wire insulation. Fluorine compounds are ineffective flame inhibitors because these compounds and their possible breakdown product hydrogen fluoride are too stable to interrupt oxidative chain reactions in the flame.

The only role of fluorine in the flame retardant additive field is the use of, typically, less than 0.1 % of powdered poly(tetrafluoroethylene) (Teflon) as an additive to prevent dripping, probably by a rheological effect.

Chlorine has a long history in flame retardant additives, and is now represented by the polychloroparaffins and by Dechlorane Plus®.

A usual mode of use of halogenated flame retardants is to combine them with antimony oxide, a strong synergist which works through the formation of flame-quenching antimony trichloride or tribromide, *i. e.*, a vapor-phase mechanism of action. Especially in the case of polypropylene, it is often advantageous from the standpoint of getting a good dispersion to first make a masterbatch with 50 % or more of flame retardant; the carrier can be selected for optimal compatibility with the main polymeric matrix.

Halogen-antimony flame retardant systems tend to be relatively cost-effective in polyolefins. Problems with halogenated flame retardants are high specific gravity, UV stability for some compounds and interference with hindered amine stabilizers. Environmental concerns, especially as put forth by “green” organizations, have also put pressure on this class of flame retardants. Criticisms about “toxic smoke” and environmental effects have often been misleading because of overgeneralization and lack of risk/benefit consideration.

2.4.1 Chloroparaffins

Chlorinated paraffins have long been used to flame retard rubber mine belts and other elastomers. Their advantages are low cost, ease of processing, and substantial freedom from blooming. Their uses tend to be limited by their stability up to about 230 °C but this allows use in many polyolefins. The materials of greatest utility are solids made from high chain length paraffins, optimally in the C₂₂–C₂₆ range. An improved chlorination process developed at Dover Chemical Co. using chlorination in the presence of water allows chlorination up to 73 % Cl, corresponding to a softening temperature of about 130 °C with improved thermal stability [32]. Like other halogenated flame retardants, they are synergized strongly by antimony trioxide. A typical formulation for reaching V-0 in polyethylene is 24 phr Chlorez® 700 (Dover’s most common grade for low density PE) and 10 phr Sb₂O₃. Chlorez® 700 SS, which is more thermally stable, is preferred for high density polyethylene and polypropylene. A formulation suggested by Dover for polypropylene uses 53.75 % PP, 25.00 % Chlorez 700 SS, 7.00 % Sb₂O₃, 10.00 % polyolefin elastomer, 3.00 % zinc sulfide, 0.75 % stabilizer and 0.50 % calcium stearate, to reach V-0 at 1.5 mm.

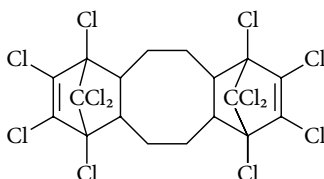
Chloroparaffins act as coupling agents in mineral-filled polypropylene and also add to the flame retardant effect of ATH or MDH. Chloroparaffins are further discussed below in connection with elastomer applications.

Besides antimony oxide, favorable flame retardant interactions of chloroparaffins with magnesium oxide and with nanoclays have been demonstrated. HDPE formulations also containing chloroparaffin, MDH and expandable graphite (discussed further below), plus possibly an impact modifier, show promise of commercial use in pallets [33].

Although lower chlorinated and shorter chain length chloroparaffins, have toxicity problems, mainly aquatic toxicity, the higher chlorinated and longer chain chloroparaffins have shown favorable toxicological and environmental results as reported by Chlorinated Paraffins Industry Assn. 2006 [34, 35].

2.4.2 Dechlorane Plus®

This is a high melting (350 °C with decomposition) solid, molecular formula $C_{18}H_{12}Cl_{12}$, chemical name dodecachlorododecahydrodimethanodibenzocyclooctene (see structure below), made by the addition of two molecules of hexachlorocyclopentadiene with one molecule of cyclooctadiene-1,5, a dimer of butadiene. It is made and sold by Oxychem. It should not be confused with an earlier product, on the market from Hooker Chemical Co. briefly in the 1960s, called Dechlorane; Dechlorane without the “Plus” designation was $C_{10}Cl_{12}$, a symmetrical polycyclic dimer of hexachlorocyclopentadiene. Dechlorane, not Dechlorane Plus, was sold in the 1960s as Mirex for bait insecticide use principally against the fire ant. Dechlorane, not Dechlorane Plus, became recognized as a serious pollutant, toxic to marine invertebrates such as crayfish. Dechlorane Plus, on the other hand, is essentially devoid of toxic properties and there is no credible evidence of environmental hazard even though its stability permits detection of traces in various environmental niches [36]. Unfortunately, the “Plus” trade name has led to some confusion of these two biologically very different compounds.



Although the main use of Dechlorane Plus is in nylons, its original use was in polyolefins, and it still finds substantial use in polyolefins, particularly where a low smoke formulation is needed. A low smoke formulation for EPDM is described by Markezich [37] as 38.2 % EPDM, 13.9 % Dechlorane Plus, 5.1 % Sb_2O_3 , 8.4 % polyethylene, 9.1 % “others” (ZnO, stabilizer, wax, coupling agent, peroxide), 25.3 % talc (zinc stearate coated), and 0.05 iron compound (smoke suppressant). This formulation gave less than one-half the smoke density of a similar formulation using decabromodiphenyl oxide in place of Dechlorane Plus. The mode of action of Dechlorane Plus involves char formation (resulting in less smoke) as well as flame inhibition, whereas the brominated additives tend to mainly cause flame inhibition.

An effective formulation for achieving V-0 at 3.2 mm in crosslinked low density polyethylene is 60 phr Dechlorane Plus, 10 phr Sb_2O_3 and 10 phr zinc borate [38].

A particularly effective use of Dechlorane Plus is in combination with a brominated additive, lowering the total additive level by taking advantage of a strong chlorine-bromine synergism [39, 40]. For example, in glass-filled polypropylene, a V-0 rating at 1.6 mm can be achieved with 50.6 % PP, 10.3 % Dechlorane Plus, 8.1 % decabromodiphenyl oxide, 10 % Sb_2O_3 , 5 % zinc borate, and 1 % Irganox 1010. The formulation retained a tensile strength of 37.3 MPa. Synergistic results were also shown for polyethylene; in a wire and cable formulation either radiation-crosslinked or not, UL-94 V-0 at 0.8 mm with no drips was achieved with 66.72 % PE, 12.7 % Dechlorane Plus, 9.78 % decabromodiphenyl oxide, and 11 % Sb_2O_3 .

2.4.3 Brominated Additives

2.4.3.1 *Decabromodiphenyl Oxide (Decabromodiphenyl Ether; Bis(Pentabromophenyl) Ether, "Decabrom")*

This is a white powder containing 83 % Br, specific gravity 3.25, and melting at around 300 °C. It is produced and sold by Albemarle as Saytex® 102E, by Israel Chemical Ltd. as FR-1210, by Chemtura as DE83R and by a number of manufacturers in the Far East. In view of the competition, "decabrom" is a low priced commodity flame retardant additive. It is probably the dominant flame retardant additive used in polyolefins, and has the advantage of good thermal stability.

In low density polyethylene (LDPE), a rating of V-2 can be reached with 6 % of decabromodiphenyl oxide plus 2 % Sb_2O_3 . Levels of at least 6 % plus 3 % respectively are recommended for linear LDPE (LLDPE) and 8 % plus 3 % for HDPE. The exact amount will be influenced by density and melt index (melt flow favors the V-2 mode of extinguishment). To reach V-0 in any of these PE types, a good starting point is 22 % decabromodiphenyl oxide plus 6 % Sb_2O_3 plus 14 % of a mineral filler such as clay or talc. In crosslinked PE, 20 % of decabromodiphenyl oxide plus 10 % Sb_2O_3 may be preferable. To get a UL-94 rating of VTM-0 in polyethylene film, or HF-1 rating in polyethylene foam, lower levels of these additives generally suffice.

In EVA, the higher the acetate content, the lower the amount of additive needed. A rating of V-0 can be reached with 35 phr of decabromodiphenyl oxide plus 17.5 phr Sb_2O_3 in an EVA with 18 % vinyl acetate but only 30 phr and 7.5 phr respectively are needed with 28 % vinyl acetate.

In PP, similar levels of addition as for PE are required. In EPDM, at least 30 % decabromodiphenyl oxide and 10 % Sb_2O_3 are recommended, and 21 % and 7 % respectively in olefinic elastomers (see more details below).

Other synergists can be helpful besides Sb_2O_3 . A formulation for a V-0 rating in low density polyethylene is 30 phr decabromodiphenyl oxide, 10 phr Sb_2O_3 , 5 phr zinc borate, and 25 phr talc. Without the zinc borate, V-2 is reached [38].

A formulation for ICL-IP for reaching V-2 in polypropylene has 4.8 % FR-1210 and 1.6 % Sb_2O_3 . This has little effect on impact or HDT. In polypropylene, to pass the UL-94 V-2 requirement at 1.6 mm, typically 3–6 % aromatic Br (such as in decabrom) must be added, along with 1–3 % antimony trioxide.

2.4.3.2 *Tetradecabromodiphenoxybenzene (Saytex 120)*

This is a white powder with mp about 380 °C, with 82 % Br. It is a more specialized additive used where very high thermal stability is needed. Although it is claimed to be useful in polyolefins, its main use is believed to be in polyamides.

2.4.3.3 Decabromodiphenylethane (Ethylenebis(pentabromobenzene), EBPB)

This is a white solid containing 82.3 % Br and melting at 361 °C. It is Albemarle's Saytex® 8010 and more recently, Chemtura's Firemaster® 2100. It can be made by direct bromination of diphenylethane [41, 42] It is fairly close in performance to decabromodiphenyl oxide but permits compounding a "PBDE-free" formulation. It also has less blooming tendency than decabromodiphenyl oxide. A comparison of this compound (EBPB), decabromodiphenyl oxide (DBDPO) and ethylenebis(tetrabromophthalimide) for reaching UL-94 V-0 and V-2 ratings is shown in Table 2.1.

Table 2.1 UL-94 V-0 and V-2 Polypropylene

Component	DBDPO	EBPB	ETBP	DBDPO	EBPB	HBCD
PP (Profax® 6523)	58	58	53	89	89	96
FR	22	22	26.9	8	8	3.2
Antimony trioxide	6	6	6	3	3	1
Talc	14	14	14			
Tensile strength @ yield, Mpa	26.2	27.6	26.9	20.0	29.6	
% Elongation at yield	4.0	3.1	2.1	5.5	6.1	
Izod impact J/m	21.4	21.4	21.4	42.7	37.4	32
Gardner impact, J/m	120	107	107	205	214	
HDT °C	71	67	66	54	53	
Melt index g/10 min.	4.6	4.1	3.9	5.7	4.8	5.3
300 hrs. xenon arc, delta E	15.1	10.0	6.6		15.1	11
UL-94 at 3.2 mm				V-2	V-2	V-2
UL-94 at 1.6 mm	V-0	V-0	V-0	Fail	V-2	V-2
Oxygen index %	26.3	25.8	25.3	24.3	25.1	

from Ref. [1]

2.4.3.4 Tetrabromobisphenol A (TBBA)

This is the largest-volume brominated flame retardant but the principal uses are as a reactive additive in epoxy circuit boards (printed wiring boards) and as an additive mainly for styrenics such as ABS or HIPS but occasionally in some polyolefins and elastomers. It is easy to manufacture and is made by many suppliers, therefore priced as a commodity. Its use as an additive is limited to low cost applications where discoloration caused by light can be tolerated. A formulation presented by ICL-IP shows that a V-2 rating could be reached by 5.2 % TBBA plus 1.7 % Sb₂O₃. The Izod impact and HDT were actually improved.

2.4.3.5 Tetrabromobisphenol A bis(2,3-Dibromopropyl ether)

This is a popular additive especially for polypropylene because of its cost/effectiveness. It is offered by Albemarle as Saytex HP-800, by ICL-IP as FR-720®, or by Chemtura as PE-68. It is a

white powder with 67.7 % Br, melting at 113–117 °C (or, some grades, lower), thermally stable at polypropylene processing temperatures, and therefore melt-blendable. Its formulations allow an improved processing rate relative to the base polymer. A typical formulation to reach V-2 is 2.2 % of this additive plus 0.8 % Sb_2O_3 . This actually increases the melt flow, and leaves the tensile, the elongation at break, and the impact only slightly decreased. To reach V-0, a formulation shown by ICL-IP uses 12 % of this additive plus 4 % Sb_2O_3 . The melt flow is still better than the base resin, and tensile strength little affected, although impact, elongation to break, and modulus are depressed. It has fairly good UV stability and can be further light-stabilized by hindered amines. This additive does have some tendency to bloom.

It is made from the relatively inexpensive tetrabromobisphenol A, which by itself is not effective in polyolefins, by way of the diallyl ether. Because half of the bromine content is aliphatic, it tends to be a more powerful flame retardant in polypropylene than a totally aromatic bromine additive, since aliphatic bromine tends to react at lower temperature than aromatic bromine. Thus, this additive allows lower loadings and consequently better physical properties. Some typical uses are in connectors and light sockets.

2.4.3.6 *Hexabromocyclododecane*

This is made by addition of bromine to cyclododecatriene, a butadiene trimer. It contains 74.7 % Br, and melts around 186 °C (not sharply, since it is a stereoisomer mixture). Its larger use is believed to be in expanded polystyrene. In polypropylene, it is melt-blendable, so could be used for example in melt-spun fiber. It is available from Albemarle as HP-900P or with a thermal stabilizer as HP-900G, and from ICL as FR-1206® or with a heat stabilizer as FR-1206® HT. The article of commerce is an isomer mixture with a melting range, differing by grades, but falling in the range of 120–185 °C. For use in polypropylene, the stabilized grades are necessary. The unstabilized material is mostly used in foamed polystyrene and textile backcoating.

2.4.3.7 *Ethylenebis(tetrabromophthalimide)*

This is Albemarle's Saytex BT-93, a yellowish powder. A whiter grade is available as Saytex BT-93W. The compound is made from ethylenediamine and tetrabromophthalic anhydride. Its Br content is 67.2 %, and its melting point is 456 °C. Despite its lower Br content than decabromodiphenyl oxide, often no more BT-93 is required to meet a given flame retardancy standard. Its principal use is for light-stable formulations in a wide variety of thermoplastics, including polyethylene and polypropylene. Another important feature of Saytex BT-93 is that it is non-blooming and suitable for heat-sealed plastics. Its wet electrical properties are also favorable for wire and cable applications. Recently, after three years of intensive study, BT-93 was removed from the UK's draft list of persistent, bioaccumulative and toxic substances.

2.4.3.8 *Bis(2-ethylhexyl) Tetrabromophthalate*

This liquid ester is available from Chemtura as DP-45 and from Unitex Chemical as Uniplex® FRP-45. It is suggested by Chemtura as a flame retardant additive for EPDM. Its main use is believed to be in vinyls.

2.4.3.9 *Tris(tribromoneopentyl) Phosphate (TTBNP)*

This compound, ICL-IP's (Ameribrom's) FR-370®, Unitex's BAP-370 is listed with the bromine additives since it has 70 % Br and only 3 % P. The phosphorus perhaps has little contribution to its flame retardancy, but serves to link the three tribromoneopentyl groups into a thermally stable, and very photochemically and hydrolytically stable, structure. It is a colorless crystalline solid with mp 181 °C. Its toxicity pattern is very favorable. In view of its light stability and melting point, it can be processed in melt-spun polypropylene as well as in molded polypropylene. A typical formulation shown by ICL-IP for reaching a V-2 rating at 1.6 mm is 2 % TTBNP and 1 % Sb₂O₃. This formulation is shown to actually increase the elongation to break.

A special grade or formulation of TTBNP is offered for the fiber application. It is ICL-IP's SaFRon® 5371 (earlier name, PR-5371), a white crystalline powder blend with 63 % Br, melting point 108–181 °C, which in PP allows reaching a V-2 rating at an additive level of about 4.8 % without the use of antimony oxide. SaFRon 5371 is also described as having excellent UV stability [43]. It can be used in outdoor or indoor stadium seats and in production of PP fibers for carpets. A patent which may be relevant shows a combination of TTBNP with a free-radical initiator such as 2,3-dimethyl-2,3-diphenylbutane (Akzo-Nobel's Perkadox® 30) and a hindered amine stabilizer [44]. The role of the free-radical initiator may be to cut the PP chains and favor melt drip; the bromine compound may make the drips non-flaming, or the free-radical initiator may activate the bromines.

2.4.3.10 *Comparison of Bromine-Containing Flame Retardants for V-2 Ratings in Polypropylene*

Several effective bromine-containing flame retardants which are available to the compounder if only a V-2 rating is needed [45] are compared in Table 2.2.

2.4.3.11 *Pentabromobenzyl Acrylate Monomer*

This monomer, ICL's FR-1025® M (the polymer is FR-1025®), is available for reactive processing into a polyolefin, to provide unextractable bromine and, in the case of polypropylene, outstanding impact properties [46]. In a suggested application, it can be compounded at 51 % by reactive processing at up to 250 °C to make an EPDM masterbatch, also containing 17 % antimony trioxide, which can then be added at 56 % to polypropylene to make a V-0 product with high impact and outstanding thermal aging properties.

Table 2.2 Comparison of Bromine-Containing Flame Retardants

Ingredients	None	Bis-dibromo-propyl ether of TBBA	Tris(tribromo-neopentyl)phosphate	Stabilized hexabromo-cyclododecane
Polypropylene	100	96	97	97.2
Flame retardant	—	3.00	2.00	2.10
Antimony trioxide	—	1.00	1.00	0.70
Percent bromine	—	2.00	1.30	1.40
Properties:				
UL-94 rating at 1/16"	NR	V-2	V-2	V-2
Melt flow rate (g/10 min.)	13	16	14	13
Tensile strength at break (psi)	2800	2800	2800	2800
Elongation at break (%)	165	140	250	285
Notched Izod (ft-lbs/in)	0.6	0.6	0.6	0.6

2.4.3.12 Poly(pentabromobenzyl) Acrylate

This is the polymer of the above-described monomer. It is available from ICL-IP as FR-1025. This polymer is especially useful in glass- or talc-reinforced PP, because it provides good coupling between the fibers or filler and the polymeric matrix. A typical formulation from ICL-IP for V-0 at 1.8 mm is 51.5 % PP, 21.9 % glass fiber, 20 % FR-1025 and 6.6 % Sb₂O₃. The melt flow is almost twice that of the same composition without the flame retardants, and the modulus and impact are actually improved. Heat deflection temperature is only depressed by 4 °C. For non-reinforced PP, a typical formulation for V-0 at 3.2 mm in a PP block copolymer is 52.9 % PP, 31.4 % FR-1025, 15.7 % Sb₂O₃.

Further advantages are that this polymeric additive is non-blooming and has good thermal aging properties. It also favors adhesion of polypropylene to glass reinforcement [47]. The cost is probably higher than most of the other aromatic bromine additives.

2.5 Antimony Trioxide

Antimony trioxide has already been discussed in context with the halogen additives. Its only use in flame retardancy is as a synergist, typically added at 3–6 % (on the weight of plastic) along with chlorinated or brominated flame retardants. It is a white powder, melting point about 656 °C. Many grades of antimony oxide are available, from many sources, differing in particle size over a range from 0.3 µm to 11 µm. They typically contain no more than 0.25–0.3 % arsenic and 0.05 % lead. The principal source is China. Because antimony trioxide may be dusty and the dust can cause some skin or eye irritation, it is common to use oiled, pelleted or masterbatched varieties.

Antimony trioxide is rated as R40 in the EU (limited evidence of a carcinogenic effect). The US EPA has not given it a carcinogenicity classification. It seems to have little ecotoxicological problem but in some jurisdictions it qualifies as a “heavy metal.” As a synergist for

halogenated flame retardants, it is difficult to find alternatives, although it can be partially replaced by zinc borates or tin compounds. Various solid formulations containing antimony trioxide combined with other inorganic additives or mineral carriers are commercially available, for example the CT FRZ series from Marshall Additive Technologies or Thermoguard CPA from Chemtura, and are found to have cost/effectiveness advantages in some halogen flame retardant formulations. Current information on toxicology and risk of antimony trioxide can be obtained from an international trade association (IAOIA) [48].

2.6 Phosphorus Additives

The main uses of phosphorus compounds in flame retardancy have been in oxygen-containing char-forming polymers such as polyurethanes, epoxies, polyamides and polyesters, where the role of the phosphorus compound is to break down to phosphorus acids which can attack oxygen functionality on the polymer, leading to char. Since this mode of action doesn't usually work well in the non-charring polyolefins, phosphorus additives have had little use by themselves. For the most part, phosphorus compounds have been used as the acid-generating part of intumescent systems where a char-forming component is also added.

2.6.1 Intumescent Phosphorus-Based Additive Systems

The overall topic of intumescent flame retardants, not limited to polyolefins, is discussed in a book by Le Bras *et al.* [49] supplemented by a further review [50]. Most of the work discussed therein is academic research. However, industrial producers of wire and cable insulating compounds continue to pursue this approach [51] with the objectives of achieving lower density, better processability and better flame retardance.

The original work on intumescent systems was directed towards fire-protective coatings to be used on wood, steel or other surfaces mainly on materials of building construction. Besides coatings, these systems have been successful in "fire stops," intumescent inserts for blocking holes and other apertures in walls. Plastics applications have been rather few because of economics (*vs.* the bromine additives), water-sensitivity, and processing difficulties. Nevertheless, much intense effort has been expended in this area by Albright & Wilson, Celanese, Montedison, Hoechst, Asahi Denka and others; perhaps, with the bromine additives and antimony oxide facing environmental concerns, phosphorus-based intumescent systems will now find more commercial acceptance.

2.6.1.1 Ammonium Polyphosphate

When ammonium phosphates are heated in the presence of urea, relatively water-insoluble ammonium polyphosphate [68333-79-9] is produced consisting of long chains of repeating $\text{—OP(O)(ONH}_4\text{)—}$ units. There are several crystal forms (type II is the least soluble) and the commercial products, available from a number of manufacturers, differ in molecular weight, particle size, solubility, and surface coating. Coated APP made water resistant by means of a durable thermoset aminoplast resin coating is available from Clariant as Exolit® 462, from Chemische Fabrik Budenheim (Germany, Spain) and from several Asian sources.

2.6.1.2 Ammonium Polyphosphate-Based Intumescent Additives

A series of compounded flame retardants, based on finely divided insoluble ammonium polyphosphate together with char-forming nitrogenous resins, has been developed for polyolefins, ethylene-vinyl acetate, elastomers and coatings. Many of these are patented by Hoechst, Celanese, Montedison, and Albright & Wilson, Asahi Denka, and others [52–55]. In most cases, the char-forming component is not explicitly identified for the individual commercial mixtures. An early Exolit IFR is believed to use tris(hydroxyethyl)isocyanurate as char former [56]. However, this additive is rather water-soluble. Some improvements in the char former involve esterifying the hydroxyethyl groups, such as by reaction with pentaerythritol spirobis(chlorophosphate) as shown in a Hoechst patent [57]. Another type of char former combination with APP is Himont's (or Enichem's) Spinflam® MF82 where the char former is a polymer with triazine rings linked by a diamine [58]. Other char-forming components used in these APP-containing mixtures may be urea-formaldehyde or melamine-formaldehyde condensation products.

Further examples of APP-char-forming mixtures are Exolit® AP 750 or AP 751 (preferred for talc or glass reinforced PP). Typical levels of addition are in the 25–30 % range to reach V-0 in polyolefins. Smoke is quite favorable compared to the halogen-antimony systems and these APP-based additives are also favorable in regard to UV stability. A limitation is that these relatively hydrophilic systems should not be used in very thin films such as < 0.5 mm or in prolonged contact with warm water. Occasional contact with water, such as rain, at ambient temperatures presents no difficulty; roof sheathing and stadium seating applications are successful. Electrical applications are the largest, however. A recent proprietary improvement, Exolit AP 760, has been introduced and this product appears especially suited for cable ducts and trays.

Other examples of proprietary formulated APP-char forming systems are Budenheim's Budit® 3077 and coated version of the same blend Budit® 3076 DCD [59]. It is said that, apart from the charring agent effect, these systems contain an additional source of NH₃ which helps to produce more voluminous char. Both grades provide a V-0 rating in PP at 27.5–30 wt. %; however, Budit 3077 falls to a V-1 level after immersion in water for 24 hours at 50 °C, whereas Budit 3076 DCD preserves the V-0 rating.

A char former which can be purchased separately and used with a phosphorus additive such as APP is an ethyleneurea-formaldehyde condensation product, Montedison's Spinflam® MF80.

2.6.1.3 Melamine Phosphates

These also have been originally developed for intumescent coatings but have found some use in polyolefins. The non-coating applications of the melamine phosphates (including the pyrophosphate but not the later-introduced polyphosphate) have been reviewed by Weil *et al.* [60]. A more recent introduction to the family of melamine salts is melamine polyphosphate, Ciba's Melapur® 200. In an intumescent formulation in a polyolefin, the melamine phosphates such as Melapur 200 can have an advantage over ammonium polyphosphate in causing less mold deposition and having better water resistance [61]. Melapur 200 probably has the highest thermal stability amongst the melamine phosphates.

2.6.1.4 *Ethylenediamine Phosphate*

This is a finely divided solid, melting point 250 °C, slightly soluble in water. It was introduced by Albright & Wilson as Amgard® EDAP and now available as Broadview Technology's Intumax® AC-3, mainly as an additive for polyolefins, EVA and PVC. Unlike ammonium polyphosphate, it is self-intumescent and does not require a char-forming synergist [62]. It is synergized by melamine or melamine pyrophosphate, and is available as a blend with these, respectively from Unitex Corp. and Broadview Technologies. There are also some further synergists, such as phase transfer catalysts (quaternary ammonium salts) or spirobisamines which in very small amounts, further enhance the action of EDAP and its melamine pyrophosphate combinations according to Broadview patent applications [63].

2.6.1.5 *Inorganic Synergists for APP-Based Intumescent Systems*

Talc or zinc borate are shown to be beneficial in some intumescent phosphorus-based systems useful in polyolefins [64].

2.6.1.6 *Other Intumescent Systems*

Efforts are made by Asahi Denka [65] to develop their family of intumescent additives, which, from patents, would seem to involve piperazine pyrophosphate or polyphosphate and melamine pyrophosphate. Their latest product, with increased stability, is FS-2 (ADK Stabilizer FP-2200®) [66]. FS-2 is effective in PP at about 20 %, and in LDPE, HDPE or EVA at about 30 %. It has heat stability to about 250 °C and allows extrusion and molding at 220–240 °C. It appears to surpass other intumescent systems in regard to much better water resistance, processability, and mechanical properties. It is more stable than a somewhat earlier product of Asahi Denka, FP-1 (ADK Stabilizer FP-2000®) [67] which suffered some decomposition under the heating effect of high shear processing.

Pre-reacted products Budit® 3118 and 3118F are available from Budenheim [59, 68] containing the phosphate structure attached to a polyol such as pentaerythritol and any acid phosphate groups neutralized by a nitrogen compound, possibly melamine. These products when used as intumescent additives can provide smoother surfaces to PP sheets and fibers.

Chemtura's (formerly Great Lakes') Reogard® 1000 and 2000 have recently been introduced commercially and are mainly recommended for polypropylene [69]. They are said to be phosphorus-nitrogen systems. These may relate to the pentaerythritol bicyclic phosphate 2:3 mixture with melamine phosphate with a small amount of a quaternary-treated montmorillonite, as disclosed in a patent application to Great Lakes' researchers [70]. At 19 % of the PEPA-melamine phosphate mixture with 0.8 % (amount critical) of the montmorillonite, a V-0 rating was obtained in polypropylene.

Another pre-reacted system which was marketed for a time by Great Lakes Chemical for use in polypropylene is the bis(melamine) salt of pentaerythritol bis(acid phosphate). This still seems to be of interest in China, as shown by a recent study [71].

2.6.2 Red Phosphorus

In polyolefins, the absence of a dehydration/charring mechanism would suggest that red phosphorus should be ineffective. However, it was found that a V-2 rating at 1.6 mm could be obtained at as low as 2.5 % by use of finely-divided red phosphorus (5 μm) [72, 73].

To avoid the handling of finely-divided red phosphorus (which is flammable as a powder!), a series of masterbatches are available from Italmatch in low density polyethylene (Masteret® 10460 B2XF and 10470), in PP (Masteret 15460B2XF and 15470) and in EVA (Masteret 40460 B2XF and 40470). The masterbatch in nylon 6,6 (Masteret 21450) is also useful in PP; the nylon provides some char which enhances the flame retardant effect. To reach a V-2 rating in PP or HDPE, loadings of only 6–7 % of Masteret 15460 B2XF are needed.

2.6.3 Other Phosphorus Additives

Recently, Italmatch introduced a colorless phosphorus-based additives, the Phoslite series [74]. One of these, Phoslite® 8361 is effective at as low as 1 % for reaching a V-2 rating in PP and thermoplastic polyolefins. The Phoslite series is believed to comprise aluminum hypophosphite and calcium hypophosphite.

The use of phosphate esters in EPDM is discussed below in connection with elastomers.

2.7 Expandable Graphite

Expandable graphite is graphite in which sulfuric acid has been introduced between the layers of the graphite structure with some oxidation of the carbon. This type of product is available from Grafftech (former Ucar Carbon Co.) as GRAFGuard®, and from Tosoh as the Flamecut® GREP® series. The acid is tightly held and does not leach out, but the lowest cost expandable graphite has an acidic character. Somewhat more expensive neutralized grades are available. Upon strong heating, as in the burning of a plastic matrix, the graphite can expand very quickly to over 100 times its original volume, producing a heat and mass transfer barrier. This barrier consists of tiny worm-like fibrils, each originating from an individual graphite particle. The effect is produced in almost any thermoplastic, and is effective in polyolefins when combined with another flame retardant such as ammonium polyphosphate, MDH, a chloroparaffin or red phosphorus. A formulation for V-0 results at 1.6 mm in EVA uses 10 phr expandable graphite and 15 phr ammonium polyphosphate [75].

In order to function, expandable graphite has to be granular, typically around 80 mesh; a very fine powder is not effective. It also produces, obviously, a black matte appearance, and makes the plastic electroconductive. It reduces impact in stiff plastics, so most uses have been in soft polymers such as elastomers. It is therefore suitable for applications where gloss, light color and electrical insulation are not considerations. Most of the interest in expandable graphite to date has been in flexible wire and cable wrappings, and in EMF-shielding gaskets where electrical conductivity is required.

2.8 Co-Additives; Hindered Amines

With many of the halogen containing additives, particularly with aliphatic halogen, some acid is usually generated in processing or later, from photodecomposition. Acid neutralizers such as calcium stearates, organotins, finely divided zinc oxide, hydrotalcite, or various other inorganic acid acceptors are added. UV stabilizers are also often added. The otherwise very-effective hindered amine types can be deactivated by salt formation with acids, so specific N-substituted hindered amine types are preferred.

In the course of studying the N-alkoxy- or N-cycloalkoxy-substituted hindered 2,2,6,6-tetramethylpiperidine types, Ciba researchers discovered that certain of them had flame retardant activity *per se*, although subsequent work seemed to lead in the direction of synergistic mixtures with many other kinds of flame retardants [76]. These compounds dissociate to free radicals upon heating, and melt flow is possibly involved in their mode of action.

2.9 Nanocomposites

One successful development of a polyolefin copolymer nanocomposite was the combination of ATH or MDH with a Südchemie quaternary-ammonium-treated montmorillonite. In EVA, this permitted lowering of the required ATH or MDH level to pass cable flammability standards from about 65 % to about 50 %, with about 3 % of the clay [77]. Thus, the formulation was substantially more flexible and thus more suitable for cable use. Extrusion speed could also be increased.

The original discovery of the value of exfoliated or polymer-intercalated layered bentonite clay (montmorillonite) in reinforcing plastics was made with nylons. It was found challenging to apply this approach to a non-polar polyolefin. Proprietary methodology developed at Nanocor Inc., provided clays, trade-marked Nanomers®, which have minimal surfactant (unlike the organoclays which often have a very high surfactant loading), and are substantially free of inorganic salt. One of the Nanomers is suitable for food packaging uses [78]. They also have stabilities to the 200–250 °C area, which gives greater processing latitude. By themselves, nanoclays do not provide flame retardancy other than the expected effect of non-combustible fillers. However, in formulations with conventional flame retardants, use of the Nanomers can lower the specific gravity (presumably by allowing a lower amount of brominated additive). The Nanomers can also replace PTFE as the anti-dripping additive. Some Nanomers are available in polyolefins as NanoMax® masterbatches. While nanocomposites alone cannot meet UL 94 ratings, combinations in PP with DBDPO and Sb₂O₃, or with Mg(OH)₂ can give V-0 ratings, can improve processing by lowering the fire retardant loading, and can provide anti-drip behavior.

A further problem with the use of natural clays as starting materials is their content of other metals such as iron, and the associated variability, color and stability effects. A few industrial groups have pursued the use of synthetic layered minerals such as magadiite, a layered sodium silicate of the approximate formula Na₂Si₁₄O₂₉·*n* H₂O [79].

Another synthetic inorganic nano-additive family has been commercially introduced by Akzo Nobel as Perkalite®. These are layered double hydroxides, mainly exemplified by magnesium

and aluminum hydroxides, intercalated with two or more fatty acid or rosin acid carboxylates. Even at low levels such as 1–5 % they substantially synergize magnesium hydroxide in polyolefins [80, 81].

Further exploration is underway of the practical applicability of carbon nanotubes (particularly multiwalled) and carbon nanofibers (lower in cost than the nanotubes) in polyethylene and ethylene copolymers containing ATH or MDH. These additives at a few percent loading favor formation of strong coherent char and thus can provide improved fire performance [82–84].

2.10 Polymer Modifications

Due to their intrinsic better compatibility with ATH or MDH, olefin copolymers such as EVA and acrylate copolymers are easier to process with these and other polar mineral additives than are the purely hydrocarbon polymers. It is also possible to increase processability by functionalizing a polyolefin by with grafted maleic anhydride. A further step which can improve performance is to crosslink the maleated polyolefin with a diamine, after fabrication of the insulated conductor. Means for doing this delayed crosslinking by use of a diamine on a “molecular sieve”, released by a hot moisture treatment, have been described [85]. Even in PE/EVA blends, the use of maleic anhydride graft polymers produces an improvement in processability, allowing for example more mineral filler such as vinylsilane-treated MDH to be loaded, as well as improving tensile strength, elongation at break and abrasion resistance [86].

2.11 Blends of Polyolefins with Char-Forming Polymers

By use of a novel compatibilization method, an alloy of GE’s poly(2,6-dimethyl-1,4-phenylene ether) (PPO), preblended with a styrenic block copolymer, can be made with a crystalline polyolefin such as polypropylene. The blends have good physical properties, good solvent (fuel) resistance, and can be flame retarded with reduced amounts of flame retardants, non-halogen, not otherwise specified, because of the char forming ability of the PPO. The preferred flame retardants are tetraphenyl resorcinol diphosphate or tetraphenyl bisphenol A diphosphate [87, 88].

2.12 Silicone Synergists

A family of polydimethylsiloxanes on silica is available from Dow Corning [89] which can reduce combustibility of a range of polymers, most effectively in combination with other flame retardants including halogen, phosphorus and metal hydroxide types. These free-flowing powders are available with functional end groups, namely amino-, epoxy and methacrylate to allow for reactive extrusion. DC 4-7081®, with methacrylate end groups, is the one recommended for polyethylene and polypropylene, even though the end groups may not be used as reactive sites. DC 4-7051 is suggested for thermoplastic elastomers. In polypropylene,

5 % of DC 4-7081 reduces heat release rate to 53.5 % of the control, and in EVA, 1 % reduces heat release rate to 66 % of control. Formation of a crosslinked siliceous surface barrier is believed to be a main mode of action; reflectivity of radiant heat from the white surface may also play a role [90].

2.13 Silicone Modification of Polyolefins by Addition or Copolymerization

A combination of chalk (calcium carbonate) and a silicone elastomer in an ethylene butyl acrylate copolymer has proven to be a good flame retardant system and has been marketed for cable use by Borealis as Casico®. The mode of action has been described [91]. Related technology where the silicon-containing group is incorporated into a ethylene butyl acrylate copolymer by use of a vinylsilane monomer is compared in a Borealis patent [92] to the addition of a silicone gum to an ethylene butyl acrylate copolymer, with either calcium carbonate or magnesium hydroxide.

2.14 Layered Polymer Approach

It was shown in a collaborative study in the UK and Hungary [93] that by layering a highly flame-retardant filled polypropylene (using MDH or Ultracarb® as flame retardants) on a non-flame-retarded or less-flame-retarded plastic layer, or using alternate layers, a flame-retardant result was obtained as good as if the entire plastic had the additive, but with better retention of mechanical properties. This approach may have broad applicability.

2.15 Specific Applications

2.15.1 Wire and Cable Insulation

Industrial cables are designed for power distribution, machinery operation, and signals. Standards in the US include UL-1072 for medium voltage power cables, and UL-1277 for power and control tray cables. Special requirements exist for plenum cables since it is important to avoid fire propagation in concealed ceiling spaces. Fire alarm cables also have special requirements to maintain signal integrity even after strong fire exposure.

An interesting statistical study [18] of ATH-MDH combinations, variously surface treated with stearic acid, vinylsilane or maleic-grafted polyethylene, in EVA led to an optimized and commercialized formulation with the following properties: density, 1.45; tensile strength, 11.7 MPa; tensile elongation, 220 %; tear strength, 7 kN/m; Durometer hardness, 94, Shore A; retention of tensile strength/elongation in 7 days at 136 °C, 116 % / 80 %; oil resistance, IRM #902 oil, 18 hrs. at 121 °C, 89 % / 98 %; fuel resistance, JP-5 fuel, 24 hrs. at 50 °C, retention of tensile strength / elongation, 65 % / 100 %; combustion properties, LOI, 37 %; toxicity index NES-413, 1.6; acidity of combustion gas, NES-754-2, pH 4.2; conductivity change, 2.3 μ S/mm; smoke index, NES-711, 15.5.

This is a major use for polyolefins. Amongst the bromine additives, for outdoor use, ethylene-bis(tetrabromophthalimide) is advantageous where light stability is a consideration. DBDPO is used in largest amounts, in view of its low cost and processing stability. However, DBDPO does have a tendency to bloom. These bromine additives are, of course, generally synergized by antimony oxide as discussed above.

Polypropylene blends with a thermoplastic elastomer plus ATH can be used in flame retardant cable, especially if the elongation-to-break is improved by use of maleic anhydride graft on PP. In a German study, good results were obtained with 10 % PP, 62 % ATH, 8 % MA-PP graft and 20 % TPE [94].

2.15.2 Wood-Polyolefin Blends

Wood plastics composites are a rapidly growing market, perhaps 20 % per year. To date, most of the applications have been ones in which flame retardancy has not been mandated. However, it has been increasingly recognized that even outdoor applications such as decking should have some degree of flame retardancy, and for indoor building materials it seems imperative. Some applications have been published such as the use of halogenated additives plus antimony oxide. It would appear that a chloroparaffin is more effective in a polyethylene-wood formulation than decabromodiphenyl oxide (Table 2.3).

Table 2.3 Formulations and Combustion Performance of Wood-HDPE Composites

Material (%)	1	2	3	4
HDPE 0.5MFI	40	30	25	30
Maple flour, 60mesh	60	55	55	55
		10	15	
Chlorez® 700S				
Decabrom				10
Antimony trioxide		5	5	5
UL94 vertical burn rating	Fails	V-1	V-0	Fails
Limiting oxygen index	25 %	28 %	30 %	28 %

(data from Dover Chemical Co., 2006)

2.16 Flame Retardant Elastomers

2.16.1 General Comments

The flame retardancy of this large and diverse category of polymers of necessity overlaps with that of polyolefins, and broadly encompasses classes of elastomeric polymers discussed in other chapters. The styrenic-butadiene copolymer elastomers are discussed in the styrenic polymer chapter. Ethylene vinyl acetate tends to behave more closely to the hydrocarbon elastomers and has been discussed with polyolefins. With the strong advent of thermoplastic elastomers, the thermoplastic and the elastomer fields are in the process of merging. However,

the flame retarding of elastomers does have some features worth a supplementary discussion in this polyolefin chapter.

Needs for flame retardancy occur in elastomeric wire and cable insulation and jacketing, conveyer belting and other belting, roofing membranes, flooring, hoses, coated fabrics, foamed rubber insulation and cushioning. Previous reviews on flame retardancy of rubbers were published by Schultz and Shen (2001) [95] and by Schultz and Dean (1997) [96]. This latter review, from the standpoint of a distributor (Harwick Standard) and a compounder (Harwick Chemical, now Excel Polymers) who specialize in the rubber industry, is particularly helpful in regard to mechanical mixing details. It also addresses the economics and reliability advantages of pre-weighed and premixed additive packages including flame retardants.

2.16.2 Diene Elastomers

The elastomers as a broad class include polymer types discussed in other chapters, and EPDM is discussed as a polyolefin earlier in this chapter. The diene elastomers constitute a large fraction of the rubber category and have a long history of flame retardant formulation which we will address here. Chloroprene (DuPont's Neoprene), a polymer of 2-chlorobutadiene, has long been used as a relatively flame resistant rubber, as are chlorinated and chlorosulfonated polyethylene.

Natural rubber and polybutadiene have a heat of combustion rather similar to the polyolefins. However, vulcanization provides crosslinks which are a predecessor to charring. The uncured polymers themselves have oxygen indices in the 17 % area and form very little char. To be flame retardant, formulations need to reach oxygen indices of at least the high 20's. Typical char yields under pyrolysis conditions for SBR, NR and polybutadiene are less than 4 %. On the other hand, from vulcanized rubber tires, under comparable conditions, char yields are in the 32–42 % area, suggesting a large contribution from carbon black plus the vulcanization system [97]. As a rule, the more crosslinks there are in a cured rubber, the higher the oxygen index (the less flammable) but even a hard rubber will burn in air. A basic study [98] showed that the oxygen index of *cis*-1,4-polyisoprene increased with crosslink density for both peroxide-crosslinked and sulfur-vulcanized rubbers, but the sulfur-vulcanized rubber showed a much sharper rise.

Systematic studies of the effect of crosslink density of polybutadiene, SBS, *k*-resin (25 % butadiene and 75 % styrene) [99], polyisoprene and polychloroprene [100] was done in Belarus and at Marquette University. It was found that in general char yield increases with increasing of density of crosslinking, however it was also noticed that thermal stability, *e.g.*, temperature of the initial decomposition may decrease at high crosslink density. Only polyisoprene showed simultaneous increase of thermal stability and tendency to char with increasing of density of cross-links.

A moderately favorable effect of carbon black on flammability was shown by limiting oxygen index of *cis*-1,4-polyisoprene vulcanizates, in a basic study in Poland [101]. The effect was greater, the higher the surface area of the carbon black. On the other hand, carbon blacks of high surface area tend to prolong afterglow combustion. This can usually be counteracted by including borates or phosphates.

Interestingly, and possibly of practical importance, it was shown in a basic study in Korea [102] that incorporation of ground tire rubber by itself or as a supplement to other flame retardants (such as red phosphorus or expandable graphite) can reduce flammability in butadiene-acrylonitrile rubber foam.

In a basic study in Poland [103], the inclusion of acrylonitrile with butadiene in the polymerization, to make nitrile rubbers such as Perbunan®, decreased flammability, as measured by limiting oxygen index, but increased visible smoke.

2.16.3 Chloroparaffins in Elastomers

Two classic approaches to flame retardancy of rubber are incorporation of a halogen-antimony system and incorporation of a water-generating heat-sink additive such as ATH or MDH. Often, these two systems are used together. A “standard package” may be 15–20 phr of chloroparaffin (70 % Cl, a solid chloroparaffin). An improved package to pass a more stringent test might use up to 30 phr of a chloroparaffin, 8–12 phr antimony trioxide and 50–75 phr ATH. A liquid product with 60 % Cl content was said to allow better processing. A representative formulation for conveyer belt edging (“skirtboard”) intended for use in mines is shown in Table 2.4.

Table 2.4 Representative Formulation for Conveyer Belt Edging

Ingredient	Parts by wt.
SBR	100
Carbon black	50
Zinc oxide	5
Stearic acid	1
Chloroparaffin (60 % Cl)	20
Antimony trioxide (90 % concentrate)	6
ATH	25
Sulfur	1.8
Accelerator (CBTS)	1
Accelerator (TMTM)	0.25

Formulation from Akrochem.

Stable solid chloroparaffins like Dover’s Chlorez® 700-SS are also useful in cable and roofing elastomers. A typical formulation is 40 phr Chlorez 700-SS, 10 phr Sb₂O₃, 60 phr paraffinic oil, 125 carbon black, 5 % zinc oxide, 0.7 phr Sulfasan® R (vulcanizing agent), 1 phr sulfur, 2 phr TMTP, and 0.3 Methyl Zimate. After vulcanization, this formulation provides a V-0 rating.

The liquid chlorinated paraffins act as plasticizers as well as flame retardants, and are often preferred for less flexible rubbers such as SBR and polychloroprene, but they are not very compatible with EPDM. The resinous 70 % Cl content chloroparaffin is probably the most used in elastomers, having broad compatibility with a wide range of rubbers. It helps on flow

and does not deteriorate physical properties, and it is usable up to about 30 % in EPDM if well dispersed. Good dispersion is also important for getting good flame retardant action.

Antimony oxide (trioxide unless otherwise stated) is typically used at about $\frac{1}{4}$ – $\frac{1}{3}$ the level of the chloroparaffins. To avoid skin irritation from antimony oxide, a concentrate in rubber or chloroparaffin may be used. The use of antimony oxide generally increases smoke and replacing part of the antimony oxide by zinc borate to reduce smoke (and often to reduce cost) is a common practice.

2.16.4 Zinc Borates in Elastomers

As discussed earlier, the most widely used zinc borate is $4\text{ZnO} \cdot 6\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ (Rio Tinto's Firebrake® ZB, available from several other suppliers), which is often used synergistically with ATH or MDH, with which it sinters and forms a barrier, and, as discussed earlier, it also releases water with heat absorption at 325 °C. In a typical rubber, 150 phr of ATH and 10 phr of zinc borate can be as effective as 190 phr ATH. Zinc borate also performs well in halogen-antimony systems, it allows replacement of some or most of the antimony oxide, and can form a glassy inorganic char with antimony oxide. Zinc metaborate, $2\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Marshall Additive Technologies' ZB200) is also used and is sometimes lower in cost.

2.16.5 Bromine Compounds in Elastomers

Bromine-containing additives have been used in SBR, natural rubber, polychloroprene, EPDM and other elastomers for wire and cable insulation, belts, tubing, seals, roofing, and coated fabrics. These additives are generally used with antimony oxide synergist, and sometimes with smoke suppressants such as a borate, stannate or molybdate. The levels of addition are generally lower than needed with chlorinated additives, and consequently physical properties are well maintained.

However, most of these brominated additives are solids which do not melt at elastomer-compounding temperatures, so that a thorough mixing is needed. Consequently it is helpful to charge the retardant early in the mixing sequence before any rubber-softening ingredients are added. Two mixing passes or predispersion may be helpful. Clays, silica or talc can have favorable effects on flame retardancy. Carbon black can cause extended afterglow in some tests and may need addition of a borate to suppress this. ATH usually has a favorable effect but calcium carbonate, magnesium hydroxide or carbonate may interfere with the action of the brominated flame retardant. Non-phosphate plasticizers will generally require more flame retardant.

Decabromodiphenyl oxide (Albemarle's Saytex 102E, Chemtura's DE83R and ICL Industrial Products FR-1210) is effective in almost all elastomers, generally with antimony oxide. It is both efficient and inexpensive, and has good high temperature resistance. This additive does have a discoloration tendency when exposed to light, but this is often not a consideration in elastomers. Recent bromination process techniques for increasing purity (avoiding lower brominated analogs) have been patented by Albemarle [104–106] and Chemtura [107].

Ethylenebis(tetrabromophthalimide) (Albemarle BT-93) is more expensive but has advantages of better light and heat stability, and less blooming tendency. In EPDM blended with

low density polyethylene, 30 phr of BT-93 and 10 phr antimony oxide gave a V0 rating and lower levels could reach the wire insulation rating of VW-1. By contrast, 30 phr of chloroparaffin and 10 phr of antimony oxide was required to reach VW-1 and V0 was not achieved. Lower smoke compared to decabromodiphenyl ether is sometimes found with BT-93.

Decabromodiphenylethane is close to decabromodiphenyl ether in performance but avoids some environmental concerns about brominated diphenyl ethers, and has somewhat better thermal stability than the ether.

2.16.6 Phosphorus Compounds in Elastomers

Phosphate esters are often used, although relatively poor at plasticizing most types of rubber. The best flame resistance but the poorer plasticization is with the triaryl phosphates, such as tricresyl or isopropylated triphenyl phosphate (such as ICL-IP's Phosflex® 41L). Chemtura recommends the more highly isopropylated triphenyl phosphate, Reofos® 95, for EPDM cable application. An example of an EPDM formulation from FMC (1993) for cable sheathing is 15 phr triaryl phosphate, 10 phr paraffin oil, 150 phr ATH, 25 phr MDH, and 25 phr magnesium carbonate. Crosslinking by dicumyl peroxide increases the flame resistance. The better plasticizer action and better low temperature stiffness is provided by 2-ethylhexyl diphenyl phosphate (Ferro's Santicizer® 141, ICL-IP's Phosflex® 362), isodecyl diphenyl phosphate (such as Ferro's Santicizer® 148, ICL-IP's Phosflex® 390) or other long chain alkyl diphenyl phosphates. These phosphates are highly compatible at levels of 15–20 phr with natural and most synthetic rubbers such as SBR, polychloroprene and nitrile rubber (NBR). Non-polar elastomers such as EPDM will “bleed” the phosphates at above about 10 phr. Since the triaryl phosphates have higher flame retardant efficacy than the alkyl diphenyl phosphates, they are more permissive of back-blending with non-flame-retardant plasticizers and oils.

Red phosphorus, stabilized and coated, has been shown by Pirelli Cable [108] to be useful in a variety of elastomeric matrices suitable for cable insulation. A representative formulation in an EVA (19 % VA) was 15 phr Masteret 40470 (a 68 % red phosphorus content), 15 phr melamine phosphate, 1.5 phr zeolite 4A and 60 phr magnesium hydroxide, to obtain insulation which passes IEC 332/1 after 5 reignitions.

2.16.7 ATH and MDH in Elastomers; Low Smoke Formulations

Elastomers can tolerate ATH or MDH loadings of 60 % or somewhat higher without loss of useful properties although hardness is obviously increased. ATH is substantially less costly but limits processing temperatures to below about 200–220 °C. A combination of roughly equal amounts of ATH and MDH will often be found more effective in flame retardancy than either alone. This apparent “synergism” may simply be the result of the endothermic water release occurring over a wider temperature range. Many varieties of both ATH and MDH are available, and have been characterized in our earlier polyolefins discussion. Particle size has some effect — smaller is somewhat better in some fire tests, but smaller particles also increase viscosity more. Dispersion is important, and can be made better by use of surface treated (stearic acid or silane) ATH or MDH. Silane treatments can also improve tensile, abrasion, electrical resistance and water-swelling resistance.

ATH or MDH are usually used at levels up to 180 phr, often with zinc borate at about 10 phr. A low smoke formulation using EPDM giving an oxygen index of 36 is shown in the Table 2.5.

Table 2.5 Low Smoke EPDM Formulation

Component	Parts by wt.
EPDM	100
Magnesium hydroxide	145
Zinc borate	10
Peroxide curing agent (DDPH)	6
Triallyl cyanurate (crosslinker)	1
Wax	3

In a low smoke formula, carbon black and petroleum oil should be minimized. A tight cure is advantageous. Dispersion of all the ingredients is important. One study showed that by having 1 phr of stearic acid to help the mineral dispersion, the oxygen index was raised from 24.5 to 34.

Calcium carbonate can also be beneficially added to non-halogen formulations since it acts as an inert diluent. It can be antagonistic in some halogen-based systems. Favorable smoke suppression results are sometimes seen. Because of its low cost, it is generally worth a trial.

Very detailed study, with copious properties data, is available from Bayer on ATH-based formulations in EVA for cable applications (Meisenheimer 1994)[109]. This study shows that 120 phr of ATH (Apyral 40) can suffice to flame-retard, but to obtain good physical properties such as elongation to break, 50–60 phr of silica treated with selected silanes or combinations of silanes is needed.

Ethylene acrylic elastomers respond well in flame retardance to the addition of high levels of ATH, and provide an unusually low smoke density as well as retaining useful physical properties over a wide range of temperature.

2.16.8 Clays in Elastomers

Elastomers such as EPDM can tolerate high loadings of mineral fillers such as clays without loss of useful properties such as flexibility. If electrical properties also need to be maintained, specific clays are advantageous on resistance and power loss. Certain clays found particularly useful in power cable because of low power loss are Engelhard's Translink® 30 (a titanate-treated calcined kaolin) and Burgess KE® (also a calcined kaolin), the low power loss being attributed to high amorphous content. At high loadings, clays provide reduced flammability simply due to fuel dilution, and to some extent, a mass-transfer barrier effect. With addition of further flame retardants, such as a melamine salt and or a char-forming polymer (GE's polyphenylene oxide for example), a substantially flame-retardant formulation can be reached [110].

2.16.9 (Poly)chloroprene and other Halogen-Containing Elastomers

Polychloroprene (such as DuPont's Neoprene) contains about 40 % chlorine in a thermally stable backbone structure. It has a long history of use for applications requiring flame retardancy, such as conveyer belts, mass transit vehicle interiors, and electrical insulation and jackets. A book was published by DuPont in 1963 on Neoprene [111]. Typically, the formulation will contain 5–15 phr antimony trioxide, 5–15 phr zinc borate and 15–40 phr ATH. Where a soft formulation is desired, a lower molecular weight Neoprene can be included, and chlorinated paraffins and/or phosphate ester plasticizers can be included.

A typical formulation [112] for polychloroprene is shown in Table 2.6.

Table 2.6 Representative Flame Retardant Polychloroprene Formulation

Component	Parts by wt.
Polychloroprene	75
Low m.wt. polychloroprene	25
Antimony trioxide	15
Zinc borate	10
Alumina trihydrate	30
Magnesium oxide	4
Hard clay	20
Carbon black	5
Ethylenethiourea (vulcanizing agent)	0.5
N,N'-diphenyl-p-phenylenediamine	2

In a formulation designed to be low in smoke, such as required for mine conveyer belts, the antimony oxide should be lowered and the zinc borate raised.

2.16.10 Chlorinated and Chlorosulfonated Polyethylenes

These elastomers tend to have some inherent flame retardancy but where this must be increased in order to pass the VW-1 requirement for wire and cable, the usual approach is to use antimony oxide (up to 5 phr) and ATH (20–50 phr; high loadings of ATH are likely to be tolerated). Clay and talc are helpful in lengthening ignition time. An intumescent flame retardant system for chlorinated polyethylene elastomer uses a phosphate foaming agent (such as an ammonium phosphate or polyphosphate), chlorowax, pentaerythritol (char former), magnesium hydroxide, antimony oxide and expandable graphite as disclosed in a 2004 patent [113].

For ratings such as UL 94 V0 in chlorinated elastomers, less than 10 phr of decabromodiphenyl ether, BT-93 or Saytex® 8010 may suffice and, indeed, may allow omission of antimony oxide.

2.17 Future Trends

Although polyolefins and elastomers pose more of a challenge to flame retardancy because of their high heat of combustion and poor char formation, a wide variety of effective flame retardant systems are available. The challenge to the compounder is to meet flame retardancy requirements with acceptable retention of useful properties and at acceptable cost. The application of a systems approach (optimizing combinations of additives) and the use of synergism, many examples of which have been cited above, appear to offer useful solutions. Statistical design of multivariate experiments seems advisable, using designs which uncover interactions [114].

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3 Polystyrenes and Thermoplastic Styrene Copolymers

3.1 Introduction

In the present chapter, we will cover each main type of styrenic, including high impact polystyrene and foamed polystyrene. Styrene-butadiene elastomers are discussed in the chapter on polyolefins and diene elastomers. Other reviews on styrenic flame retardancy published in recent years have encompassed the theory as well as mixing and test methods, rather than focusing on the retardant chemicals [1, 2]. The present authors have reviewed this topic with inclusion of theory and academic or non-commercialized industrial work [3].

3.2 General Comments on the Fire Properties of Styrenic Polymers

Polystyrene and its copolymers have the tendency to depolymerize when exposed to fire temperatures, and the volatile products are materials of high fuel value, namely styrene monomer, styrene dimers and related hydrocarbons such as benzene, lower-alkylbenzenes, and a few percent of oxygen-containing related aromatics [2]. Polystyrenes, unless blended with char-formers, by themselves form little or no char [4]. The volatiles burn with copious soot formation. In the vicinity of a polystyrene fire, visibility can be nil. Moreover, while depolymerization is taking place, melt flow and drip are also occurring, and the drips may be capable of igniting other flammable objects. If flaming drips are allowed by the test standard, as in the UL-94 V-2 rating, then the dripping may actually be useful to meet flame retardancy requirements.

It is possible to retard the vapor phase combustion reaction by means of additives which reach the flame zone. These will be discussed in more detail below. For many uses of styrenics, especially electrical equipment, the requirements are to prevent a small source of ignition, such as a hot or sparking wire, from igniting the item, or if ignited, causing it to self-extinguish quickly. The UL 94 test is the dominant one in the US and indeed in much of the world, although other small scale tests are also significant.

Styrenic polymers that will be discussed in this chapter include polystyrene itself, the copolymers with other vinyl monomers such as acrylonitrile and butadiene, and the impact modified (high impact, HIPS) which is generally a grafted blend of a rubbery polymer.

Styrenic polymers fall into several main subclasses: polystyrene itself as molding resin; high impact (rubber modified) styrene copolymers (two main subclasses: HIPS and ABS), and expandable polystyrene (foam). Two other types of styrenic polymers, namely, the blends of HIPS with PPO and the blends of ABS with polycarbonates, have their own combustion characteristics, mainly because of the char-forming PPO or PC components, therefore we are discussing them elsewhere in this book.

Where properties of the additive or formulation are stated without reference, the information was taken from the manufacturers' product literature.

3.3 Crystal Polystyrene

This is nearly pure polystyrene and is primarily used in food containers, compact disk boxes, and miscellaneous housewares where flame retardancy is not required. Where flame retardancy is required, a soluble bromine compound is usually used, typically hexabromocyclododecane. A recent patent [5] also suggests the use of pentabromobenzyl bromide.

3.4 Expandable Polystyrene and Extruded Polystyrene Foam

There are two main technologies used to make polystyrene foams. One, expanded polystyrene (EPS) involves the preparation of polystyrene beads containing a blowing agent, typically a lower alkane, the beads are then placed in a mold or void to be filled, and expanded by heat. Extruded polystyrene foam (XPS) involves the expansion of a melt, containing the blowing agent and any other desired additives such as a flame retardant, through a slotted die from whence it expands. The processing temperature is somewhat higher for XPS than for EPS so that a somewhat higher stability requirement is imposed on the flame retardant system for XPS. It is convenient to add the flame retardant to the styrene before polymerization, but it must not interfere with polymerization and cause a high concentration of residual styrene, or, in the case of XPS, it must have enough thermal stability to survive the extrusion process.

Expanded polystyrene foam is a major material used for insulation of buildings, refrigerators, and the like. The maximum flame-spread and smoke-developed ratings at a maximum 4" (102 mm) thickness and 4.0 lbs./cu.ft. (64 kg/m³) density are less than 25 and 450, respectively, as measured by the ASTM E-84 25-ft. tunnel. This and various other standards allow styrenic foam to melt and flow when exposed to fire, provided that the drips are not burning, and melt-flow can be exploited as a mode of flame retardancy. Because some pyrolysis to monomer and dimer takes place, aside from the flow of molten polymer out of the fire zone, a vapor-phase flame retardant is often needed. The patent literature shows that this retardant is almost always a brominated aliphatic compound which can readily release HBr (a vapor-phase flame retardant). At the relatively low processing temperatures for foamable polystyrenes, these aliphatic bromine compounds are generally stable enough. And, with fast enough HBr release, a synergist such as antimony trioxide is not needed and generally not used.

The leading brominated additives actually used are as follows.

3.4.1 Hexabromocyclododecane (HBCD)

HBCD (Albemarle's Saytex HP900 powder or granules, HP900HG granules, and 9006L ground particles or ICL-IP's FR-1206), made by addition of bromine to cyclododecatriene, a product of catalyzed trimerization of butadiene. It is a mixture of three diastereoisomers, with one (the gamma-isomer) comprising 80 % of the technical product. The structures

have been elucidated by nmr and X-ray crystallography [6]. There are some differences in stability of the isomers [7] and presumably the manufacturers have tried to optimize the process to favor stability at processing temperatures. This matter is complicated by the fact that there is a thermal isomerization process which interconverts between diastereoisomers [8] and this conversion occurs during compounding. Generally, HBCD is not used with antimony oxide.

There are many special grades of hexabromocyclododecane. Saytex HP900SG and BC-70HS are blended with stabilizers for use in XPS and injection molded HIPS, and allow better color stability of the resin. BC-70HS appears to be more highly stabilized and is targeted for use in HIPS (see section below on HIPS). Some of the stabilizer systems for HBCD have been disclosed and claimed in patents, for example a combination of a dialkyltin dicarboxylate and a barium or cadmium carboxylate [9]. The use of a zeolite in the range of 0.6–1.2 %, optionally with a zinc salt of a fatty acid, is also patented as a means for stabilizing a HBCD formulation [10]. The systematic development of an optimized stabilized HBCD using two stabilizers is described by ICL Industrial Products (ICL-IP former Dead Sea Bromine Group) [11]. Other stabilizers mentioned [2] are metal hydroxides, metal oxides and hydrotalcite.

HBCD has shown bioaccumulation tendencies in the environment [12, 13]. A risk assessment under EU auspices is still underway as of 2008; a preliminary report was rather inconclusive [14]. No risk was identified for manufacturers or users. Brominated flame retardant industry is implementing Voluntary Emissions Control Action Program (VECAP) which helps decreasing further emission of HBCD in the environment [15]. Research by users and flame retardant manufacturers is underway to find substitutes.

Hexabromocyclododecane particles can be coated with a resin to make them insoluble in styrene, and can then be added into the styrene polymerization stage. The coating seems to improve the foam structure, reduces the water content of the foam, and improves dimensional stability [16].

3.4.2 Tetrabromocyclooctane

This compound is Albemarle's Saytex BC-48, made by addition of bromine to cyclooctadiene, a product of catalyzed dimerization of butadiene. This compound is more easily soluble in the polymer than hexabromocyclododecane and lower processing temperatures can be used, in the 150–160 °C range. It has found only minor usage, mainly in styrenic foams, textile coatings, solvent-based paints and hot-melt adhesives.

3.4.3 Dibromoethyldibromocyclohexane

It is Albemarle's Saytex BC-462 made by addition of bromine to vinylcyclohexene, a product of the Diels-Alder dimerization of butadiene. It also is more soluble in the polystyrene, and is used where the expandable polystyrene is processed in the 150–160 °C range. It is somewhat less volatile than tetrabromocyclooctane.

Thermal stabilization of brominated aliphatic or cycloaliphatic flame retardant additives for styrenics, exemplified by tetrabromocyclooctane or dibromoethyldibromocyclohexane

is shown to be accomplished by addition of a thermoplastic acrylate or methacrylate, in the 5–10 % range relative to the bromine compound. Optionally, hydrotalcite is also added [17].

3.4.4 Other Bromine Flame Retardants

Chloropentabromocyclohexane is made by addition of bromine to chlorobenzene (Dow 651). This was at one time a leading additive for expanded polystyrene foam, but appears to have been discontinued.

Certain other brominated compounds were in use for a time but appear to have been discontinued, such as cinnamalacetophenone tetrabromide [18]. A few other bromine compounds have been recommended for this use in patents, and, if the leading additive HBCD is viewed as an unfavorable risk, one or more of these may be revived. At this time, the authors are not aware of the current commercial use of these additives. For instance, hexabromohexene [19], 1,2-dibromoalkyl ketones [20], 1,1,2,3,4,4-hexabromo-2-butene [21], dialkyl tetrabromophthalate [22], bis(2,3-dibromopropyl) tetrabromophthalate [23], 2,4,6-tribromophenyl allyl ether [24] and bis(allyl ether) of tetrabromobisphenol A [25].

A more likely substitute for hexabromocyclododecane, judging from a series of Albemarle patent applications, is N-(2,3-dibromopropyl)-4,5-dibromotetrahydrophthalimide [26–28]. For a time, tris(2,3-dibromopropyl) phosphate was used, but this compound was shown to be a mutagen and was discontinued in the mid-1970s.

More recently, it was shown that non-brominated polystyrene can be blended with a flame retardant amount of a brominated anionic styrene polymer plus a bis(pentabromophenyl) ethane to make extruded flame retarded foam [29]. The use of a polymeric or oligomeric additive is often considered more environmentally benign than the use of migration-capable small molecular weight additives.

A substantial patent literature exists on the use of combinations of brominated additives in expandable polystyrene. Combinations of the usual bromoaliphatic flame retardant with a more thermally stable bromine compound with an aromatic, vinylic or neopentyl structure may permit a lower total loading of flame retardant [30].

3.4.5 The Flammability Effect of the Expanding Agent

The expanding agent is often a flammable hydrocarbon, such as pentane, and there is a problem in the use of ethyl chloride or other halogenated blowing agents. Some combinations of fluoro- or fluorochloroethanes with alkanes have been patented [31].

A patent to Hoechst [32] suggests that there may be need for a storage period of extruded polystyrene foam, depending on dimensions, before it will pass flammability tests, and they claim shortening this period by use of less than 1.9–3 % propane/butane mixture. It is not clear how general these constraints may be.

3.4.6 Synergists with Brominated Additives in Polystyrene Foam

Along with the brominated additive, certain synergists are used. An early example is 0.25–0.75 phr of an allyl ether, said to aid in the decomposition of the bromine compound

during burning [33]. The use of peroxy compounds or other free-radical-forming compounds with labile C—C, O—O or N=N bonds, to enhance the action of the brominated flame retardants has been known and used for a long time, since some early work of Dow [34–38]. An advantage in efficiency was claimed by applying the radical-generating synergist to the outside of the polystyrene particles while having the bromine compound distributed throughout [39]. Peroxides useful in this mode of synergism must not decompose at processing temperatures, but must decompose at the temperatures reached by the molten polymer when exposed to flame: examples are dicumyl peroxide (Hercules' Dicup® R), 1,3-bis[2-*t*-butylperoxy]isopropyl]benzene (Akzo Nobel's Perkadox® 14) or 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane (Arkema's Luperox 101). With care to feed the peroxide so as not to decompose it prematurely, combinations of HBCD with di-*tert*-butyl peroxide (Trigonox® B) or *tert*-butyl hydroperoxide (Trigonox® A80) can be used [40].

A non-peroxide synergist which can be used is one which undergoes C—C bond cleavage to produce tertiary-alkyl radicals, such as 2,3-dimethyl-2,3-diphenylbutane (Akzo Nobel's Perkadox® 30).

Another type of synergist to be used along with the usual brominated flame retardant is a waxy material such as a chloroparaffin, melting above the foaming temperature of the EPS, at about 0.1–2 % [41].

3.4.7 Phosphorus-Bromine Combinations in Polystyrene Foam

Combinations of HBCD with a wide variety of phosphorus compounds, with examples showing the use of triphenyl phosphate, were claimed by Dow as flame retardants permitting lower levels of bromine [42].

Combinations of HBCD (or many other Br additives) with triphenyl phosphate or with encapsulated red phosphorus are disclosed as flame retardants in foamed styrene copolymers with specified olefins [43]. In extruded styrenic foam, combinations of a halogenated flame retardant with a P—N compound (such as APP), various tetrazoles and triazines, boron compounds or phosphoric esters (such as triphenyl phosphate) are disclosed for the production of flame retardant foam with certain cell dimensions [44, 45].

Achievement of improved flame retardancy of a EPS while reducing the amount of HBCD to less than 2.5 % is made possible by the use of 0.1–4 % of a phosphorus co-additive, exemplified by triphenyl phosphate and various other phosphates, phosphonates, phosphinates, phosphines, phosphonium compounds or phosphine oxides [42].

3.4.8 Non-Bromine Systems in Polystyrene Foam

Alternatives to the bromine additives have been disclosed in the patent literature. Very high loadings of ATH, such as 150–250 phr, afford a flame retardant foam and it is surprising that densities lower than 100 g/l can be thus obtained. Further addition of phosphorus or brominated flame retardants is recommended to reach adequate flame retardancy [46].

The use of heat-set flame-resistant carbonaceous fibers derived from polyacrylonitrile or pitch has been claimed as a flame retardant method for foams, including polystyrene foams.

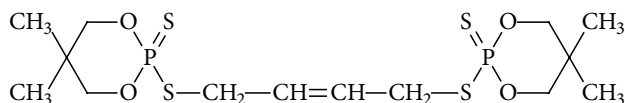
The fibers appear to collect at and protect the surface [47]. The use of carbonaceous particles or platelets is similarly disclosed by the same inventors in a later patent [48].

Graphite particles of 1–50 micron size can also be used, particularly in combination with a high percentage Br additive, such as HBCD, to obtain flame retardant EPS foam with density of equal or less than 35 g/l [49]. Expandable graphite plus a halogenated flame retardant and optionally antimony oxide are disclosed for flame retarding EPS [50].

A combination of 1–12 % expanded graphite and a phosphorus flame retardant (exemplified by red phosphorus and/or triphenyl phosphate) can enable EPS of 20–200 g/l and cross-sectional area of at least 50 cm², to be self-extinguishing [51].

A combination of less than 2 % elemental sulfur plus a phosphorus additive (exemplified by triphenyl phosphate, triphenylphosphine oxide or sulfide, or hexaphenoxyltriposphazene) afford higher oxygen indices, up to 26, in polystyrene such as the type used in foam production [52].

A 2008 patent application [53] with many Dow inventors covers a wide range of thiophosphates and dithiophosphates, most examples having neopentylene rings, such as



The applications exemplified are in foamed polystyrene.

Extruded polystyrene foam can be made flame retardant by use of a blend with an epoxy resin containing reacted-in DOPO and phosphoric acid [54]. Another way of increasing flame resistance of EPS is to make a board with a flame-resistant barrier, such as a coating, laminate or foil [55].

A novel way of making a flame retardant polystyrene foam is to coat the beads before expansion with a boric acid plus a binder. After expanding, the boric acid forms a vitreous coating when the foam is exposed to flame [56].

A patent application by Owens-Corning inventors [57] claims that nanoclays such as sodium montmorillonite in a carrier such as water are useful to improve fire performance of a foamed polystyrene.

3.4.9 The Recommended Fire-Safe Use of Extruded Polystyrene Insulation

Ample directions are available from Dow and other manufacturers regarding the safe use of polystyrene foam insulation. Some of the key points are:

Polystyrene foam boards should be separated from the interior of a building by a code-compliant thermal barrier such as ½" thick (12.7 mm) gypsum wall board applied with code-compliant fasteners. More details as to the various styrene foam insulation boards and their recommended applications are available from Dow and ICC [58].

Expanded polystyrene foam is highly useful for rooftop applications, withstanding foot traffic and weathering. In order to be used directly on steel roof decks, the proposed configuration

must pass UL 1256 or FM 4450. Large scale tests have been done by Underwriters Laboratories with favorable results [59].

At least one application has had an adverse fire experience and is advised against. The US Coast Guard recommends that foamed polystyrene insulation not be used in commercial fishing vessels for example as engine box covers, since in this high heat location, the foam could ignite and spread fire rapidly with dense smoke [60].

3.5 High Impact Polystyrene

Polystyrene produced by polymerization, with some grafting, in the presence of rubber latex particles, is known as “high impact polystyrene” (HIPS). HIPS is used widely in equipment enclosures such as TV sets, computers, business equipment housings, and other electrical equipments. The TV set use is probably the largest application. In the US, this application requires a UL-94 V-0 rating, whereas in Europe a typical level of flame retardancy is about in the range of a UL-94 HB [61]. Recent publicity about the high rate of fire deaths from TV fires in Europe (contrasting with a low rate in the US, where fire standards for TV sets are more stringent) may stimulate a higher level of flame retardancy in Europe. Flame retardant HIPS has an attractive balance of mechanical properties, processability and cost.

3.5.1 Bromine-Containing Flame Retardants for HIPS

Approximately 10 wt. % Br in combination with antimony oxide is required to pass UL94 V-0 requirements. The exact amount will vary with the rubber content of the HIPS. HIPS is usually processed at 220–230 °C, so thermally stable bromine compounds are favored.

3.5.1.1 Decabromodiphenyl Oxide (Ether) in HIPS

DBDPO, Albemarle's Saytex 102, ICL-IP's FR-1210, Chemtura's DE-83 (also available from Chinese manufacturers) is the most widely used flame retardant for HIPS. Its high bromine content (83 %) and low cost make it a favorite choice. It is a stable solid up to its melting point of 305 °C. It is soluble in hot molten HIPS and only partly phase-separates on cooling, thus reduces impact only slightly but lowers HDT somewhat more [62]. It does have a tendency to yellow when exposed to ultraviolet light (such as sunlight) and therefore is mainly used in painted or dark pigmented plastic. DBDPO is typically used at about 12 % with about 4–5 % antimony trioxide as a synergist. A formulation in HIPS with 6 % rubber content with 12 % DBDPO and 5 % antimony trioxide is reported to have a LOI of 25.3 and a UL-94 rating of V-0, notched impact of 43 kJ/m (without fire retardant., 85.9) and Vicat softening point of 91.5 (without fire retardant, 92.5).

This photosensitivity not only causes discoloration but interaction of DBDPO (and in the same way, tetrabromobisphenol A) with wavelengths in the 260–280 and 300 nm range can also provoke polymer chain degradation to some degree [63]. Light stabilizers can make some improvement; in one extensive study [64], 0.25 % of a chlorobenzotriazole photostabilizer plus 0.25 % of a particular hindered phenol radical inhibitor were found most effective

in preventing darkening, and could be further boosted by an epoxy cresol novolac or zinc stearate or tin maleate. A hindered amine photostabilizer also was effective in such combinations.

However, the use of dark pigments is the most effective and economical means. If this approach is unsuitable, then it may be necessary to turn to the more expensive more-light-stable brominated additives such as Albemarle's ethylenebis(tetrabromophthalimide) (BT-93), to light-stabilized Saytex® 8010, to ICL-IP's tris (2,4,6 tribromophenoxy) triazine or to tribromophenyl end capped brominated epoxy oligomers discussed further below.

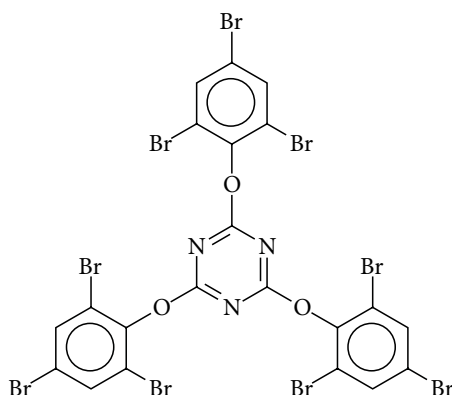
DBDPO has been under attack as a hypothetical environmental problem (to a large extent "guilt by association" with pentabromodiphenyl oxide which does migrate badly). However, a recently issued 10-year study done for the EU concluded that DBDPO does not appear to present a significant risk to humans or to the environment [65]. Further support for this position is based on studies done by the US EPA and by the US National Academy of Science. A further consequence of this recognition is that DBDPO was exempted from the EU Directive 2002/95/EC on the Restriction of Hazardous Substances (RoHS) used in electronic and electrical applications. This conclusion was disputed (2006) by Denmark and various Green organizations. Arguments are presented pointing to some evidence of degradation in the environment to less innocuous lower brominated diphenyl ethers. In 2008, a European court ruling has the effect of banning the electrical and electronic use of DBDPO in the EU after July 1, 2008 [66].

3.5.1.2 1,2-Bis(pentabromophenyl)ethane

It is Albemarle's Saytex® 8010 and Chemtura's Firemaster® 2100. It is a high melting solid (melting point 350 °C) which has a use pattern similar to that of DBDPO. This is useful for customers who wish to have formulations totally free of all brominated diphenyl oxides. It has some other advantages such as superior UV resistance relative to DBDPO and low blooming tendency. It is suitable for HIPS systems where recycling is anticipated. A disadvantage of Saytex 8010 relative to DBDPO is somewhat poorer impact in HIPS, but this can be corrected for by either adding an impact modifier or starting with a higher impact grade of HIPS.

3.5.1.3 2,4,6-Tris(2,4,6-Tribromophenoxy)-1,3,5-Triazine (ICL-IP's FR-245)

This compound is also a high melting (230 °C) but melt-blendable solid with a pattern of utility rather similar to DBDPO but with advantages of better melt flow, impact and light stability [67, 68]. Some comparative data is shown in Table 3.1.

**Table 3.1** V-0 and V-2 Formulations of FR-245 in HIPS

Composition (wt.%)	HIPS, no FR	HIPS V2	HIPS V0
HIPS	100	88.4	77.8
FR-245	—	8.9	14.9
Sb ₂ O ₃	—	2.4	4
UV absorber	—	0.3	0.3
TiO ₂	—	—	3
Bromine content %	—	6	10
FR UL 94	not rated	V2	V0
GWT 960C	fail	pass	pass
Melt flow, g/10 min 200 °C 5 kg	5	8	15
Maximum strength, MPa	19	21	22
Elongation at break, %	61	53	47
Modulus, MPa	1600	1700	1800
Izod notched impact, J/m	130	120	115
HDT (1.82 MPa, annealed)	78	76	76
UV stab., ΔE 300 hr xenon	8	10	11

From ref. [66]

A combination of this melt-blendable flame retardant with a filler-like flame retardant such as bis(pentabromodiphenyl)ethane enables molding of large dimension housings of electronic equipment made of HIPS, without the problems of melt flow and poor impact (Table 3.2).

Another advantageous combination of FR-245, as claimed by Daiichi, is with tris(2,3-dibromopropoxy) cyanurate [69].

Table 3.2 Melt Flow and Impact Properties of FR-245 Based HIPS

Flame retardant	MFI at 200 °C, 5 kg	Gardner Impact kg-cm
FR-245	10	100
1:1 FR-245/Saytex 8010	8	81
Saytex® 8010	5	62

3.5.1.4 Modified Brominated Epoxy Oligomers (MBEO)

These are melt-blendable additives especially suitable for HIPS and ABS. They provide excellent flow properties with good light stability. However, for demanding applications with large dimensions, high impact styrenic copolymers flame retarded with MBEO's have rather inadequate impact. Partially replacing MBEO with FR-245® retains the good melt flow but greatly improves the impact.

3.5.1.5 Hexabromocyclododecane

HBCD of the ordinary grade suitable for expandable polystyrene is not quite stable enough for the temperatures commonly encountered in extruding and injection molding, typically up to 220 °C. A stabilized version of HBCD is available from Albemarle as Saytex BC-70HS; it has been targeted for use in injection molded HIPS that must pass the IEC 695-2-1/2 glow wire test from 750 to 960 °C. At 5–7 % loading, without antimony oxide, injection molded HIPS can pass this glow wire test with burning times of less than 10 seconds, and can reach UL-94 V2 rating (1.6 and 3.2 mm). This additive also can be used in crystal polystyrene. Another stabilized version of HBCD is Albemarle's Saytex HP900SG. As mentioned, a risk assessment on hexabromocyclododecane is underway (2005-8) under EU auspices.

3.5.1.6 Tetrabromobisphenol A

TBBA (Albemarle Saytex RB-100 or CP-2000 or 's FR-1524) is a lower melting solid, often used as a reactant in epoxies or polycarbonates, but also used as an additive to a limited extent in HIPS and mostly in ABS. Because of its lower melting point, it melts into the polymer, aiding melt flow considerably, and allowing impact to be maintained. Another advantage is low cost. On the negative side, it is poor on color stability and tends to be used only in dark formulations.

3.5.1.7 Tetrabromobisphenol A Bis(2,3-Dibromopropyl Ether)

This product (Albemarle Saytex HP800A or the granular version HP800AG, and ICL-IP's FR-720) is a relatively low melting solid, melting point 108–120 °C, rather soluble in HIPS and suitable for reaching UL-94 V-2 ratings. It has minimal effect on impact strength. Probably, its larger uses are in polypropylene.

Another stable aliphatic bromine compound (actually a blend) with 56 % Br and melt range of 187–240 °C is available as Albemarle's BC-56HS. This has good UV resistance and good

thermal stability, a favorable feature if recycling is anticipated. A recent Albemarle patent application gives a clue that the blend may be a brominated cycloalkane with an acrylate polymer which acts as a stabilizer [17].

3.5.1.8 1,2-Ethylenebis(tetrabromophthalimide)

This additive, Albemarle BT-93, is used when discoloration must be minimized. UV stability is its outstanding feature, but it has a slight yellow color to begin with. A colorless version is a purified grade, BT-93W. BT-93 has a melting point above the processing temperature of HIPS and is quite insoluble in HIPS. It acts like an inert filler, and therefore tends not to lower HDT, but on the other hand, is somewhat detrimental to impact strength [62]. An alternative way to achieve good UV stability in a flame retardant styrenic is to use FR-245 or Saytex® 8010 with a good UV stabilizer system.

3.5.1.9 Comparison of Typical Formulations of Brominated Flame Retardants in HIPS

Table 3.3 shows a comparison of several of the above-discussed bromine-based flame retardants for HIPS.

Table 3.3 Performance of Some Brominated Flame Retardants in HIPS

Additive	Control	BT-93 ethylenebis (tetra-bromo- phthalimide)	8010 bis(pentabromo- phenyl)ethane	CP-2000 tetrabromo- bisphenol A
Flame Retardant:	0.0	18.0	14.6	20.4
% Antimony trioxide	0.0	4.0	4.0	4.0
% Bromine	0.0	12.1	12.0	12.1
Physical properties				
Izod Impact 3.2 mm, ft-lb/in	3.3	0.6	2.0	1.7
Izod Impact 3.2 mm, J/cm	176.	32	107	91
DTUL 3.2 mm °C	79	82	80	68
MFI 230 °C/3800 g	5.8	3.3	2.6	14.0
UV Stability				
100 hr Xenon arc	7.9	7.3	21.1	nd (bad)
300 hr Xenon arc	9.2	9.4	25.3	34.3

(from Albemarle)

Various other polybrominated additives are shown in recent patents to be useful in HIPS, bis(pentabromobenzyl) ether for example [70].

3.5.1.10 *The Dripping Problem and Antidripping Additives*

Many thermoplastics, and HIPS is no exception, can have flaming drips. In some end-products, it is acceptable to have drips if they are non-flaming, but flaming drips can be tolerated only in those products allowed to pass UL-94 with a V-2 rating. The contribution to fire safety of V-2 standards is controversial. Where the stricter V-1 or V-0 standards are required, means must usually be found to prevent drip. The addition of very small amounts of polytetrafluoroethylene (PTFE) powder, at loadings generally in the 0.01–0.1 % range, are often effective, probably because of a rheological effect. Uniform and continuous mixing of such small quantities of a powder is challenging.

As a means to reduce dripping, where it cannot be allowed, flame retardant systems involving modified grades of brominated epoxy polymer with built-in antidripping properties ICL-IP's SaFRon 5500 series may be used. Incorporating the antidrip additive allows higher fire retardant efficiency so that lower loadings can be used, allowing adequate impact strength and also good light stability. A typical non-dripping V-0 formulation is 82 % HIPS, 13.8 % SaFRon 5526, 2.5 % Sb_2O_3 , 2.5 % TiO_2 and 1 % UV stabilizer [71]. ICL-IP discontinued SaFRon 5526 and replaced it by SaFRon 5531 which is similar.

3.5.1.11 *The Effect of Brominated Flame Retardants and Antimony Oxide on Mechanical Properties of HIPS*

An academic study [72] showed that the impact strength of HIPS declined gradually and approximately linearly as the loading of DBDPO was increased. Antimony oxide, used as a synergist, did likewise, but it was found that Sb_2O_3 particles at 0.08 micron size did not reduce impact strength, but in the range of 0.5–1.2 microns, severe impact strength loss occurred. However, at 4–10 microns, once again, no impact strength loss occurred. It was postulated that these larger particles served as craze terminators.

A study of the effect of particle size, using representative solid additives showed that impact strength of a polystyrene can even be increased by particles several microns in diameter because of formation of voids, peeling layers and extension of crazes [73]. However, some compounders believe it best to have smaller particles, and in the case of antimony oxide, often the flame retardant effect is improved by using smaller particles. The detrimental effect of powdered additives on impact strength can also be at least partially overcome by starting with a "superhigh" impact plastic, or adding an impact modifier, such as a chlorinated polyethylene (which also contributes to flame retardancy), a thermoplastic styrene-butadiene-styrene block polymer, or ethylene-vinyl acetate. Where the use of very fine particles adversely influences processing characteristics, a surface-modifying agent ("coupling agent") may help.

Liquid flame retardants generally do not lessen the impact strength and may, in fact, often improve it.

A useful study was done at Monsanto addressing the quantitative relationship of solubility of decabromodiphenyl oxide in HIPS to the impact and processing characteristics [74].

Regarding electrical properties, usually the bromine-antimony systems have somewhat decreased loss factor, and may be prone to leakage currents and diminished arc resistance, particularly on aging [2].

3.5.2 Non-Halogen Flame Retardants for HIPS

This is a challenge because of the need to avoid spoiling impact strength, heat distortion temperature and cost. Noting that UL 94 V0 can be obtained for PPO-HIPS, researchers have studied the use of smaller loadings of PPO plus the char-forming phosphates. This system can also be aided by adding char-forming phenolic novolacs [75] or by adding small amounts of “nanoclay” (an exfoliated layered montmorillonite). For example, a formulation of 80 parts by weight of HIPS, 20 parts PPO, 20 parts of resorcinol bis(diphenyl phosphate) and 3 parts of quaternary amine-treated montmorillonite can give a V-0 rating [76].

A patent shows the use of expandable graphite plus a phosphorus flame retardant, such as resorcinol bis(diphenyl phosphate) or triphenyl phosphate, plus a co-additive, such as 12 wt. % of a polycarbonate, to prevent migration of the phosphorus compound to the surface of HIPS [77].

A US patent application [78] by Israeli inventors shows HIPS flame retarded to V-0 by 15 % expandable graphite and 15 % melamine.

A US patent application [79] by Cheil (Korea) shows HIPS flame retarded by a combination of an aryl phosphate such as PX200® and a phosphonate such as Amgard® 1045.

3.6 Flame Retarded Acrylonitrile-Butadiene-Styrene Copolymers (ABS)

Compared to HIPS, ABS is more costly, has somewhat higher heat distortion temperature, substantially greater impact strength and more solvent resistance. It is easily molded, has high gloss, and combines high toughness with flexibility. ABS is available in a wide range of properties. It is used in automotive parts, electrical apparatus and various consumer disposable products.

Non-flame-retarded ABS pipe (Schedule 40 pipe), can be used in many building construction applications, such as in “non-rated construction” (single family dwellings), and, if properly installed, even in some fire-rated construction. Producers of ABS pipe point out that it starts to melt and collapse long before it ignites. In fire-rated construction, NBS tests show that it will not spread fire or smoke where it penetrates a non-combustible wall if properly installed. Firestop caulks, sealants collars and the like with an adequate F rating in accordance with ASTM E-814 must be used. It is pointed out, also by the ABS pipe manufacturers, that in the installation of the competing metallic piping, the plumbers’ torch and lead pot actually pose a serious hazard.

However, the use of non-flame-retardant ABS pipe in construction is not without controversy, particularly where codes require materials with a E-84 tunnel rating of less than 25. Favorable conclusions regarding this application have been published in the US [80] but unfavorable conclusions in Canada [81].

Where flame retardancy is required, namely in electronic equipment enclosures, brominated additives are most commonly used. It is important to find a suitable balance of impact strength, heat distortion temperature, melt-flow index, color stability, and cost. Usually tensile strength and flex properties are not much affected by the additives.

3.6.1 Brominated Flame Retardants Used in ABS

The leading flame retardant is tetrabromobisphenol A (TBBA, Albemarle RB-100 or CP-2000, Chemtura BA-59P, ICL-IP's FR-1524). This is the largest volume bromine flame retardant, but a major part of it is used in epoxy resins as a reactive. Its use as an additive in ABS, often synergized by Sb_2O_3 , is favored by low price and processing ease. It can be processed in ABS up to about 220 °C. It is not recommended where high impact or high heat distortion temperature are needed. About 4 % of the plastics in automobiles (2003 information) is ABS, used in dashboard and light fixtures [82].

The use of tetrabromobisphenol A has been the subject of an eight year evaluation under the EU Risk Assessment procedure which reviewed over 460 studies. The human health report was finalized in May 2005 and concluded that no health effects have been identified. Some environmental risk was noted with free TBBA (*i. e.*, TBBA not bound in epoxy resin) in sludge applied to agricultural soil, an unlikely occurrence [83].

Tetrabromobisphenol A can only be used in darker shades of ABS or in painted products because of its photoinstability. A study of it in polystyrene showed that wavelengths of 260–280 and 300 nm were most active and caused not only color change but some polymer main chain cleavage [84].

Some synergism has recently been claimed to occur in ABS flame retarded by tetrabromobisphenol A and antimony oxide by the further addition of a styrene-maleic anhydride copolymer grafted with a titanate coupling agent LICA 44 (Kenrich Chemical Co.) [85].

Another highly effective and commercially-used flame retardant for ABS is bis(tribromophenoxy)ethane (more precisely, 1,2-bis(2,4,6-tribromophenoxy)ethane) (Chemtura's Firemaster FF-680). This solid, melting point 223–228 °C, provides a good balance of impact strength and heat deflection temperature, and low cost. However, it does have some tendency to bloom.

Another ether made from 2,4,6-tribromophenol is the tris(tribromophenoxy)cyanurate (2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine) (ICL-IP's (former Dead Sea Bromine Group) FR-245), discussed above in connection with HIPS. This solid, melting point 230 °C, with 67 % Br, has high melt flow during injection molding, very low vapor pressure and therefore it is free of any tendency to bloom and has good UV stability, good impact and heat distortion temperature in ABS. Formulations using FR-245 in ABS are shown in Table 3.4.

FR-245 has a very favorable impact strength rating, over twice as high, *vs.* bis(pentabromophenyl)ethane (Albemarle 8010) by the falling ball test.

A family of oligomeric polyethers made from tetrabromobisphenol A and epichlorohydrin has been developed by ICL-IP. The preferred one for use in ABS is F-2016, which is a solid melting at 105–115 °C. Being rather high in molecular weight and having negligible volatility, it is non-blooming. It also has good UV stability. Some of these oligomers have a problem with metal adhesion, which can be overcome by use of a tribromophenol-end-capped version,

Table 3.4 V-0 and V-2 Formulation of FR-245 in ABS

Composition (wt. %)	ABS, no FR	ABS V2	ABS V0
ABS	100	87.5	79.4
FR-245	—	8.6	14.3
Sb ₂ O ₃	—	3.6	6
UV absorber	—	0.3	0.3
TiO ₂	—	—	3
Bromine content %	—	6	10
FR UL 94	not rated	V2	V0
GWT 960 °C	fail	pass	pass
Melt flow g/10 min 220 °C 10 kg	10	19	21
Maximum strength, MPa	44	44	43
Elongation at break, %	19	13	6.3
Modulus, MPa	2100	2300	2200
Izod notched impact, J/m	211	163	131
HDT (1.82 MPa, annealed)	93	93	93
UV stab., ΔE 300 hr xenon	4	7	9

From ref. [66]

F-3020, which also has improved UV stability. On the other hand, F-3020 does cause some loss of Gardner impact.

Some proprietary modified grades of these tribromophenol-end-capped polyethers marketed under the SaFRon 5500 series trade name, have built-in antidripping properties, better Gardner impact, and even some enhancement of flame retardant properties allowing lower bromine and antimony loadings. A typical V-0 formulation in ABS would be 75.7 % ABS, 17.4 % SaFRon 5526, 3.4 % Sb₂O₃, 2.5 % TiO₂ and 1 % UV stabilizer [86]. Another variety is SaFRon 5520 which is recommended for UV stable ABS and enables more than a five-fold increase in Gardner impact compared to F-3020 [87]. Recently ICL-IP discontinued SaFRon 5520 and 5526, but it is offering SaFRon 5531 with similar properties.

A patent application by Korean inventors [88] suggest that with a variety of brominated flame retardants (exemplified by decabromodiphenylethane) with antimony oxide in ABS, the use of a small amount in the 1 phr range of a stearate or ethylenebisstearamide is beneficial to flame retardancy by drip enhancement.

Where high light stability (color stability) is needed, the additive of preference is ethylenebis(tetrabromophthalimide), Albemarle's BT-93, or even better, BT-93W, which is a purified version of BT-93. Besides good light stability, these additives resist bloom and plate-out. They do tend to reduce impact, and may be compensated for by impact modifiers. They are also more costly than most other ABS flame retardant additives.

A comparison of some of the principal brominated flame retardants used in ABS is shown in Table 3.5.

Table 3.5 Performance of Some Brominated Flame Retardants in ABS

Component	Tetrabromo- bisphenol A	Brominated epoxy oligo- mer F-2016	End capped brominated epoxy oligo- mer F-3020	Tris (tribro- mophenyl) cyanurate FR-245
ABS	76.8	73.7	75.9	79.4
Flame retardant	17.2	20	17.8	14.3
Antimony trioxide	6	6	6	6
UV absorber	—	0.3	0.3	0.3
Properties:				
UL-94 class (1.6 mm)	V-0	V-0	V-0	V-0
MFI (220, 10 kg) g/10min	52	39	28	21
Tensile max., MPa	39	41	41	43
Elongation at break, %	6.7	2.5	3.5	6.3
Modulus, MPa	2 400	2 400	2 300	2 300
HDT, °C	86	91	91	93
Notched Izod, J/m 23 °C	100	65	92	131
UV stability, ΔE 300 hrs	— (poor)	3	8	9

Data from [82]

3.6.2 Chlorinated Additives for ABS or HIPS

A unique chloroparaffin with a high softening point, 160 °C, Dover's Chlorez 760, can be used in styrenics, such as ABS and HIPS, but processing temperature should be 220 °C or less. A small amount of chlorinated polyethylene can also be helpful as a processing aid and flame retardant adjuvant in many styrenic systems flame retarded with bromine additives.

A high melting cyclic chlorohydrocarbon, Oxychem's Dechlorane Plus, melting point 350 °C (with decomposition) and a chlorine content of 65 %, is useful in HIPS and ABS to meet a UL94 V-0 rating, and has its advantage in respect to low smoke and better photochemical stability than decabromodiphenyl ether. It can be synergized with antimony oxide but for lowest smoke, ferric oxide or zinc oxide are preferred [89]. Also, Dechlorane Plus can be used in a moderately synergistic combination with a bromine additive plus antimony oxide. A V-0 rating at 1.6 mm in HIPS uses 78 % HIPS, 9 % Dechlorane Plus, 10 % of a brominated epoxy additive, 3 % of antimony trioxide; the formulation gives a Notched Izod impact of 89 J/m; interestingly, the addition of 1 % of a silicone-silicate such as GE's SFR-100 raises the impact to 106 J/m [90–92]. Dechlorane Plus formulations tend to produce some char which may show afterglow; this can be overcome by including some ammonium polyphosphate or ATH in the formulation.

A significant commercial use for Dechlorane Plus is in light-colored HIPS television enclosures, used with antimony oxide. An improved formulation, in respect to impact and afterglow, uses a combination of 90 % Dechlorane Plus and 10 % chlorowax (70 % Cl). An advantageous

formulation uses 70.9 % HIPS, 18 % of a 90 % Dechlorane Plus-10 % chlorowax mix, 4 % Sb_2O_3 , 5 % SBS impact modifier, and 2 % SFR-100 silicone and 0.1 % Teflon gives a V-0 at 1.6 mm and a notched Izod of 134 J/m [89].

Formulations of ABS designed to optimize particular product properties can be achieved by combinations of the various halogenated flame retardant additives; in summary, tetrabromobisphenol A is favorable for flowability, but inferior for impact, HDT and stability), Dechlorane Plus is favorable for HDT and stability but inferior for impact and flowability, Firemaster® FF-680 is favorable for impact strength but inferior for HDT, and brominated epoxy is favorable for HDT and stability but inferior for impact [91]. Acceptable compromises may be attainable by use of combinations.

3.6.3 Non-Halogen Flame Retardants for ABS

ABS-polycarbonate blends are an important family of engineering thermoplastics, which can be flame retarded very well with aromatic diphosphates. They are discussed in Chapter 7.

ABS-poly(ethylene terephthalate) (PET) blends can be flame retarded to a V-1 level by including a char-forming phenolic novolac. For example, a formulation of 65 parts ABS, 35 parts PET, 3 parts phenolic novolac and 20 parts resorcinol bis(diphenyl phosphate) (Fyrolflex® RDP) can reach V-1 according to Cheil (Korea) workers [93].

A US patent application [78] by Israeli inventors shows ABS flame retarded to V-0 by 15 % expandable graphite and 15 % melamine cyanurate.

3.7 Flammability Requirements and Tests

There are many tests and methods that have been developed to study flammability. A brief summary is given in Chapter 12. For a more complete world-wide overview, the reader is referred to Troitzsch's monograph, recently revised [94]. Only those which are important for flame retardant styrenic polymers are mentioned here, in connection with each flame retardant. Some of these tests are regulatory requirements for specific applications, while others are mainly for research purposes. The flame retarding of styrenic polymers is often done to pass a specific test; the formulation needed to pass one test may be quite different than that required for another test.

Note that those tests which allow passing by melt-flow and dripping favor flame retardants, usually soluble ones, which do not form char. Formulations of this type can often be defeated by solid additives such as mineral fillers or even pigments.

3.8 Mechanistic Considerations as a Guide for Flame Retardation of Styrenics

As mentioned previously, when polystyrene is subjected to temperatures of a flame it pyrolyzes by a depolymerization mechanism to give monomer, oligomers and other aromatic cracking products [95]. Very little char is formed. The burning of these volatile products in

the vapor phase supplies heat back to the solid or molten surface (the “condensed phase”). The aromatic structures of the fuel are able to condense to large polycyclic structures, resulting in a very sooty flame. If the thermal energy from the flame, which is transmitted mainly by radiation, secondarily by convection or conduction, is sufficient to maintain the pyrolysis and vaporization of the pyrolysis products, the flame will sustain itself even after the ignition source is removed. In order to flame-retard a plastic such as a polystyrene, this cycle must be somehow interrupted, either in the vapor phase or condensed phase, or both. Flame retardants may act in either the vapor or solid (condensed) phase, or both.

This cycle may be oversimplified, and two aspects which could be important are often overlooked. First, in burning configurations where oxygen can reach the surface, as in upward burning of a vertical surface, exothermic oxidation in the condensed phase may also be providing energy. Secondly, the radiant energy from the flame must usually pass through the “dark zone” consisting of outflowing pyrosate, and substantial endothermic dissociation may be taking place in that zone. This part of the flaming process has been little investigated.

3.8.1 Vapor Phase Mechanisms in Styrenics and Some Implications

A detailed discussion of flame chemistry and its inhibition is outside the scope of this review, and the reader is referred to a mechanism review by Lewin and Weil [96] as well as to Fristrom’s book on flame chemistry [97]. A recent study on aliphatic bromine compounds in polystyrene shows not only the effect of flame poisoning but also the effect of melt flow, and the effect of synergists specifically antimony oxide and talc [98].

3.8.2 The Smoke Problem with Styrenics

Whether or not they are flame retardant, styrenic polymers burn with a very smoky (sooty) flame. The typical flame retardants working in the vapor phase, by inhibiting the combustion chemistry, generally increase the smoke yield. However, it should be kept in mind that to whatever extent the flame retardants prevent the styrenic polymer from igniting and propagating a flame, the net yield of smoke may be lower. Thus, there is some possibility of confusion. It is quite possible the continuous stream of smoke in an apparatus where the combustion is driven by continued application of heat, as in the cone calorimeter, both the continuous smoke and the total smoke will be worse in the presence of the flame retardant, but on the other hand, in a test configuration where the igniting flame is removed and the polymer is allowed to self extinguish, *total* smoke may be less in the presence of the flame retardant because less material is burned.

The decision as to whether the increased rate of smoke production is a problem may hinge on whether the expected ignition source is a small flame, temporarily applied, or whether the styrenic polymer is exposed to an ongoing fire where other materials are burning.

Attempts to reduce the smoke yield have been made by means of additives. Unlike the case of PVC, where good smoke suppressing additives have been found and commercialized, no such smoke suppressant for styrenics has been found.

3.8.3 Condensed Phase Mechanisms in Styrenics

There are a number of flame retarding mechanisms that operate in the solid phase of polymers. One of these depends on additives that absorb some of the heat of combustion by endothermic reactions; this was mentioned in the previous section in connection with metal hydroxides.

Formation of a protective char layer is another important condensed phase mechanism. Unfortunately, polystyrene does not form any appreciable levels of char during burning even in the presence of charring catalysts. There has been some academic progress made in enhancing char formation of polystyrene by the use of Friedel-Crafts chemistry, but this involves building in specific functional groups. Manufacturers have not done this.

Intumescence is the formation of a foamed char, which is a particularly good heat insulator. Intumescent packages generally contain a source of carbon to build up char (carbonific), a compound which generates an acid upon heating in the flame, and a compound that decomposes to generate blowing gases to generate the foamed char [99]. The acid is required to cause charring of the carbonific component. A limitation of this approach is that relatively high levels (30 wt. % or more) of the intumescent package are required to flame retard styrenic polymers.

The formation of a barrier film on the surface during burning is another mode of action, which may in fact be part of the mechanism of action of phosphorus-based flame retardants, which can form polyphosphoric acid on pyrolysis. This action also has not been well studied.

Another mechanism that can be used in the condensed phase is to use an additive that enhances decomposition, and thus dripping, of the polymer during burning. This may be desirable for achieving a UL 94 V-2 rating, but may not be an option for a V-0 requirement. Promoting non-flaming drips is one way to make nylon polymers V-0, but this approach is not used for styrenic polymers other than expandable foams.

3.9 Summary and Future Trends

Flame retardant styrenic polymers find utility in applications such as building insulation (expanded polystyrene foam) and electronic enclosures (flame retardant HIPS, ABS and styrenic blends). The most effective flame retardants are halogen (particularly bromine) containing compounds, these flame retardants act by inhibiting the radical combustion reactions occurring in the vapor phase. The state of flame retardant plastics is in a state of flux, due to influences of regulatory and environmental factors. There are movements to discontinue use of halogen containing flame retardants, but at the present time it is difficult to find cost effective non-halogen alternatives for styrenic polymers other than for their blends containing char-forming components.

The value of having a flame retardant in styrenics, such as in TV enclosures, has been shown by a careful life-cycle study balancing fire risk against environmental risk [100]. European statistics show very substantial life-saving benefits from the use of flame retardants. Moreover, once the environmental risk from fire products such as polycyclic aromatic hydrocarbons is taken into account, the environmental balance also appears favorable for the flame retardants.

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4 Flame and Smoke Retardants in Vinyl Chloride Polymers – Commercial Usage and Current Developments

4.1 Introduction

Polyvinyl chloride (PVC) is the world's third largest plastic in terms of sales. Its success is the result of low price, extraordinary versatility and stability to weathering. By the use of plasticizers, its hardness and flexibility can be varied over a wide range. It is largely used as a homopolymer but the vinyl chloride-vinyl acetate copolymer is also of significance, and chlorinated PVC is important in pipe and conduits. The topic of flame and smoke retardance of PVC has been reviewed by Nass and Heiberger [1] in a 4-volume encyclopedia published in 1997. An updated book, edited by Grossman, was published in 2008 covering broadly the formulation aspects of PVC [2]. The present authors published in 2005 an update of the literature (scientific as well as patents) on flame retardancy and smoke suppression in PVC [3]. Another overview was presented in 2006 by Shen [4]. The fire performance of PVC was reviewed by Hirschler [5] in 2005 who provides authoritative and detailed discussion of standards, test methods, and performance of PVC in many important tests. Therefore, we will put most of our emphasis on the flame and smoke suppressant additives themselves.

In this chapter, as in the rest of the book, information not specifically referenced has been derived from commercial product literature. Since the authors are located in the US, materials available in North America are emphasized, but we must note that European and Asian producers and vendors exist for virtually all of these additives.

PVC does not exist as the pure substance other than at a polymerization site. Neat PVC, *i. e.*, rigid or unplasticized PVC, is difficult to ignite, and will cease burning as soon as the source of heat or flame is removed. Neat PVC has 56.8 % chlorine content and an oxygen index of about 47, compared to most non-halogen polymers, which have oxygen indices ranging from 17.4 (polypropylene or polymethyl methacrylate) to 26 (polycarbonate). Even in dry powder form, PVC is ignition-resistant, relatively safe to air-convey without serious risk of dust explosions unless admixed with more combustible powders. The fire behavior of PVC has been extensively studied. When PVC is thermally decomposed or exposed to flames, it dehydrochlorinates and the chlorine content gets converted to hydrogen chloride gas, which can be emitted into the vapor space or retained in the condensed phase if a base such as calcium carbonate is present to produce calcium chloride. However, unlike carbon monoxide, the hydrogen chloride concentration quickly declines as it is absorbed on surfaces, and it usually does not travel far [5]. The relative importance of the various fire gases in real fires is discussed by Hirschler [5].

Unplasticized PVC softens as it is heated and as it burns. Generally it is difficult to ignite and readily self-extinguishes. The net heat of combustion is 16.9 kJ/g, whereas most other plastics

are in the range of 24–43 kJ/g. The minimum radiant flux for ignition is about 21 kW/m². The self-ignition temperature is 507 °C. Hydrogen chloride gas begins to be evolved at in the 227–277 °C range for pure PVC; but this temperature is greatly affected by stabilizing or destabilizing additives. Because of its high content of chlorine which is a non-contributor to the heat of combustion, the heat release characteristic of unplasticized PVC is the lowest of all commodity plastics. Also, the flame spread rates of rigid PVC formulations are much lower than wood and most other polymers, for example as measured by the ASTM E 162 or E 84 test methods [5].

Unmodified PVC is a stiff brittle material and it is never used as an uncompounded polymer. Rigid PVC formulations (*i. e.*, with 0 to about 10 phr plasticizer) generally require processing aids, stabilizers and often impact modifiers such as acrylate-elastomer shell-core copolymers. Rigid PVC finds use in pipes, pipe fittings, extruded profiles for gutters, siding, window frames, fencing, decking, electrical equipment housings, blister packages and thermoformed containers. In building applications, PVC is probably the most widely used plastic. It has reasonably good ultraviolet light stability (dependent on pigment) and fair heat stability. Its softening temperature can be raised by blending, for example, with ABS or ASA. In terms of the flame spread test ASTM E-84 (Steiner tunnel) used for building code requirements in the US, rigid PVC achieves a flammability rating of Class 1, *i. e.*, a flame spread index less than 25, compared to the reference for wood which is rated at 100. However, the smoke developed index of rigid PVC tends to be poor, unless smoke suppressant additives are used, as discussed below. For many applications, there are no flammability or smoke regulations, or such lenient standards that the usual PVC formulation is adequate.

A rather new use for rigid PVC (and other plastics) is in pallets, as a replacement for wood. The flammability requirements for this application tend to be based on the fire performance of wood. Because of the stacking of pallets in warehouses and storerooms, there should be stringent flammability requirements, which are likely to favor PVC over other inexpensive plastics, but requirements seem not to be fully in place as yet.

PVC compounds (semi-rigid and flexible) are now extensively used for cable jackets and even primary electrical insulation. Such compounds can be used for the relatively demanding plenum applications, where they must meet the requirements of the UL 910 test, recently replaced by the NFPA 262 test (which has both flame propagation and smoke limitations). This use was developed in the last two decades and has advantages in relative cost (compared to fluoropolymers), and ease of processing. The major disadvantage has been smoke obscuration and that has been met by improved additive systems. Flexible PVC systems with flame-retarding and smoke-retarding additives are discussed below.

4.2 Plasticized (Flexible) PVC

The fire properties of plasticized PVC are largely determined by the type and amount of plasticizer. The plasticized formulations comprise the largest use of PVC, for wire and cable, packaging films, flooring, upholstery, roofing membranes, wall covering, pool liners, shower curtains, apparel, greenhouses, geomembranes, automobile parts, conveyer belts, toys, and bottles. Some of these applications require flammability limitations and some have smoke

limitations as well. Typical plasticizers are dialkyl phthalates, especially “dioctyl” phthalate (more properly bis-2-ethylhexyl phthalate), diisononyl phthalate and diisodecyl phthalate. Vinyl flooring often contains butyl benzyl phthalate, which better resists the dark marks which are caused by heels. Other plasticizers are also esters; trimellitates (which have lower vapor pressure than the phthalates), adipates, sebacates, citrates, and oligomeric or polymeric polyesters [1].

The typical ester plasticizers are volatile enough to be emitted from the vinyl when it is strongly heated by a flame, and they are all flammable under these circumstances. There are two traditional approaches taken to reduce the flammability of plasticized PVC, namely, the use of antimony oxide and the use of less flammable or non-flammable plasticizers, namely phosphate plasticizers and tetrahalophthalate plasticizers discussed below. Recent trends have been in the direction of higher molecular weight, less volatile plasticizers, sometimes bromine-containing. With such approaches, the flame spread and heat release can be comparable to that of unplasticized PVC or even of fluorinated elastomers [5].

4.3 Antimony Oxide and Related Products

Antimony oxide (antimony trioxide, Sb_2O_3), although usually not effective as a flame retardant in the absence of halogen, is a powerful synergist in halogenated polymers such as PVC. It is typically used in the range of 3 to 7 phr (rarely as much as 12 phr). It is generally believed to act mainly by means of its reaction with HCl to form antimony trichloride which is volatile at fire-exposure temperatures and which acts as an active flame poison. Antimony trioxide is a stable white powder. The main source at the present time is China where it occurs as the sulfide ore, stibnite. Some production of antimony oxide occurs in North America from imported ore, but a large amount of antimony oxide is imported ready to use as a flame retardant synergist for plastics. A typical particle size range is 1.0–1.8 microns, more broadly, 0.1–2 microns. Larger particle size product is available (for example Chemtura's Thermoguard® L with a particle size of 2.0–3.2 microns) which can be used to lessen the pigmentation effect. On the other hand, the use of a fine particle size antimony trioxide can provide improved physical properties.

The pigmentation effect can be avoided by use of the more costly antimony pentoxide, a colloidal powder produced by precipitation from sodium antimonate solution. Its submicron size is too small to scatter light and thus allows for translucent or even transparent vinyl compounds, with no effect on color matching. Sodium antimonate itself can be used, with the possible advantage of lower smoke [6].

A dust problem associated with antimony oxide, occasionally causing respiratory or dermal irritation, has been solved by addition of mineral oils or plasticizers to make dust free grades, or by compounding into pelletized antimony oxide concentrates.

Various grades of antimony oxide are marketed for use in PVC. A good quality grade has uniformity of crystal size and cubic shape, which enhances dispersion, improves compounding properties and provides improved batch-to-batch consistency. Certain trace impurities, such as selenium, cause discoloration and the use of grades having high levels of these impurities should be avoided. The powdered version of antimony oxide in Europe has an “R40”

label (“limited evidence of a carcinogenic effect”), but a risk assessment is underway at the time of this review; the most current reports and the regulatory status of antimony oxide are available from the International Antimony Oxide Industry Association on-line newsletters.

Antimony oxide is also available in admixture with other inorganic materials. For example, Chemtura’s Thermoguard® CPA is a mixture of antimony oxide, barium sulfate and zinc sulfide. This product has been on the market for some decades, and offered a price advantage for some vinyl formulations. The zinc sulfide component contributes some flame retardant synergism and smoke reduction. Formulators can obtain the zinc sulfide-barium sulfate combination as lithopone which also serves as a white pigment, and can be used in addition to antimony oxide or as a partial replacement.

Various proprietary combinations of antimony oxide with zinc oxide and/or magnesium hydroxide, molybdenum compounds and other minerals are available from Marshall Additive Technologies, previously under the Charmax trade name, now under the trade name of C-TEC®. For example, C-TEC® FRZ30S and FRZ20S are 35 % and 23 % antimony oxide combinations with a zinc compound and a carrier. Such combinations can improve flame and smoke results and/or reduce formulation cost [7]. These other inorganic additives are discussed further below.

Some commercial pelletized mixtures of brominated flame retardants and antimony oxide are available and are said to avoid dust and provide easier handling.

The interaction of antimony oxide with phosphorus-based flame retardants is discussed below under the phosphates. Suffice it to say that such combinations are often used but some degree of antagonism may be found depending on additive ratios; the relationship is complex. The topic of antimony-phosphorus antagonism has been reviewed [8].

The use of antimony oxide in PVC generally elevates the smoke level relative to the mass burned in small scale tests, but on the other hand, the total smoke may be lowered in a large scale test or in an actual fire because of the reduction in the amount or rate of polymer burning. This viewpoint regarding smoke in fires is discussed by Hirschler [5].

4.4 Halogenated Phthalate Plasticizers

The principal product of this family is dioctyl (or di-2-ethylhexyl) tetrabromophthalate, available from Great Lakes Chemical (now Chemtura) as DP-45 or Unitex Chemical as Uniplex® FRP-45. It is highly effective as a flame retardant with relatively low smoke production. It is usually used in combination with antimony oxide and other additives. One advantage is that dioctyl tetrabromophthalate has very low volatility and is very thermally stable, with only 5 % weight loss at 290 °C, well beyond the processing range of PVC. It is used in high-end vinyl applications such as plenum wiring and railway passenger coach wiring. It can also be used together with the phosphate esters and Ongard® 2 (a proprietary MgO-ZnO-based composition made by Great Lakes Chemical, now Chemtura), and zinc borates. Some suggested formulations and their properties are given in Table 4.1.

Unitex claims that a mixed halogen (bromine-chlorine) phthalate ester has improved flame retardancy and mechanical properties. This is probably a blend of dioctyl tetrachlorophthalate and dioctyl tetrabromophthalate; patents to Unitex [9, 10] show that such plasticizer

Table 4.1 Properties of FR-PVC Using Dioctyl Tetrabromophthalate with 15 phr Antimony Oxide and 5 phr Pb Stabilizer at 100 Parts of PVC (Geon® 30)

Formulation	1	2	3	4	5
Dioctyl tetrabromophthalate	—	20	40	60	93.4
Trioctyl trimellitate	60	47.2	34.3	21.5	0
Tensile modulus	1640	1740	1760	1830	1980
Tensile strength (at break)	1860	1880	2050	2320	2520
Tensile elongation (%)	308	286	278	263	239
Low temp. brittleness (°C)	−22	−20	−14	−14	−6
Shore “A” hardness	88	88	88	90	92
LOI (O ₂ %)	27	31	33	36	42
NBS smoke					
Smoldering (Dmc)	200	190	180	170	140
Flaming (Dmc)	450	450	440	180	170

combinations allow improved flexibility. Some evidence for bromine-chlorine synergism has been discussed in a broad review on flame retardant synergism [8].

4.5 Chlorinated Paraffins

These are old products with recently improved stability. They are used as secondary plasticizers and as sources of supplemental chlorine content. They are also relatively low in cost compared to the flame retardant phosphate plasticizers which they can partly replace. Chloroparaffins are useful in formulating for relatively low smoke. Early versions had marginal thermal stability but newer grades from Dover Chemical have been much improved in stability by use of lower temperature chlorination conditions, choice of substantially unbranched paraffin feedstocks, and inclusion of an effective stabilizer package [11]. A typical product of this type is Dover's DG50, which has an average composition approximating $C_{14}H_{24}Cl_6$. Cost savings can also be achieved by replacing part of the antimony oxide or phosphate plasticizer in a PVC formulation by chlorinated paraffin. For example, a formulation of 50 phr dioctyl phthalate and 8 phr antimony oxide can be replaced with 40 phr dioctyl phthalate, 12 phr chlorinated paraffin and 4 phr antimony oxide, with similar performance and some cost savings. Likewise, a formulation of 30 phr calcium carbonate, 3 phr antimony oxide, 15 phr dioctyl phthalate, and 35 phr octyl diphenyl phosphate can be replaced, as suggested by Dover, with 30 phr calcium carbonate, 3 phr antimony oxide, 25 phr octyl diphenyl phosphate and 12 phr chlorinated paraffin (Dover's DG50) with cost savings but substantially equivalent physical properties. To avoid migration and exudation, the level of chloroparaffin must be limited, the limit depending on the primary plasticizer. With dioctyl phthalate, the chloroparaffin (such as Dover's DG 50) should not exceed 20 phr, whereas with diisononyl phthalate, the chloroparaffin should not exceed 16 phr. Higher levels of chloroparaffin can be used when a primary plasticizer is an aryl phosphate.

Toxicological and aquatic toxicity concerns have been avoided by the longer chain length paraffins and by chlorination to a higher level.

Polychlorinated polyethylenes such as Dow's Tyrin® can also be blended with rigid PVC to afford good low temperature impact and ductility, good retention of strength and weatherability and improved smoke without loss of flame retardancy [12].

4.6 Inorganic Flame Retardants, Synergists and Smoke Suppressants

4.6.1 Alumina Trihydrate (Aluminum Hydroxide, ATH)

This additive is part of the flame retardant system of many rigid and semi-rigid vinyl formulations. It is inexpensive on a per-pound basis but rather high loadings must be used, and its density causes the formulation to be less favorable in cost on a volume basis. It is available in a variety of particle sizes, ground varieties in various sizes ranges (for example, the Marshall Additives Technologies H-TEC ATH series which covers from 1.2–26 micron median particle size), and precipitated varieties in the 1–1.5 micron range, and with various surface coatings to aid dispersion, to reduce hydrophilicity and in some cases to get bonding to the polymer. Wire, cable and flooring formulations are its largest uses. The power cable segment is growing rapidly particularly in Asia, the telecom segment less so. ATH acts as a heat sink when the formulation is exposed to flame, by virtue of its endothermic release of water starting at about 204 °C, and consuming 1051 J/g of ATH. The released water also dilutes the organic fuel released from the formulation, reduces the oxygen concentration in the flame zone, and has a cooling effect in the flame. The layer of dehydrated alumina offers a barrier to heat and mass transfer. Frequently, this barrier is bolstered by the presence of carbonized material, and may also be improved by the presence of fluxes and sintering components such as zinc borate.

Plasticized PVC containing typical phthalate plasticizers generally produces dense smoke, although this can be alleviated by further additives, as discussed below. The smoke emission is aggravated, particularly under flaming conditions, by the presence of antimony oxide but alleviated by the addition of ATH. Interestingly, it was shown by Huber (who have both ground and precipitated ATH) that from the smoke property and oxygen index effect, it doesn't much matter whether the ATH is ground or precipitated [13].

Various other smoke-reducing additives will be discussed below. Data from Albemarle shows substantial reduction of smoke levels from PVC containing ATH, in comparison to antimony oxide formulations at the same level of flame retardancy. Obviously, to reach the same flame retardancy, the ATH percentage must be much higher than the antimony oxide percentage. There also seems to be a favorable synergism between ATH and antimony oxide in regard to smoke suppression and delay in smoke release. A study at Huber [13] shows that the optimum is in the range of 1:10 to 1:15. The same study shows that ATH can replace, entirely or partly, the expensive smoke suppressant ammonium octamolybdate. The same group also found that the combined use of ATH with calcium carbonate can maintain the oxygen index

and leaving smoke only slightly increased while reducing compound cost. Typical PVC cable formulations using ATH are shown in Table 4.2.

Table 4.2 Typical PVC Based Formulation with ATH

Components (and resultant properties)	Content (phr)	
PVC (K value = 70)	100	100
Diisononyl phthalate	55	55
Calcium carbonate (<i>e.g.</i> , Omya® EX H1SP)	10	10
ATH (<i>e.g.</i> , Martinal® OL-104E)	50	40
Antimony oxide		5
Lead-based stabilizer	4	4
Lubricant (<i>e.g.</i> , A-C 6A)	0.5	0.5
Properties		
LOI (ASTM D 2863-77)(% O ₂)	27	31
Tensile strength (DIN 53504)	17.5 MPa	16 MPa
Elongation at break (DIN 53504)(%)	220	250

Some other useful starting-point formulations are as follows: For thin rigid vinyl protective films: 100 phr PVC, 15 phr ATH or 8 phr ATH plus 2 phr Sb₂O₃ plus 2 phr Ongard® 2 (Chemtura's proprietary MgO-ZnO-based composition). For flooring: 100 phr PVC, 100 phr ATH plus 80 phr phthalate plasticizer plus stabilizer as needed. For wall covering to meet LOI of 27 %, DIN 4102: 100 phr PVC, 34 phr ATH, 20 phr phosphate plasticizer, 3 phr epoxidized soy bean oil, 1 phr Sb₂O₃, and 2 phr stabilizer. For carpet backing (PVC foam coatings): 100 phr PVC, 60 phr ATH, 80 phr plasticizer (presumably a phthalate) and up to 5 phr stabilizer. For conveyer belts: 100 phr PVC, 40 phr ATH, 10 phr calcium carbonate, 50 phr phosphate plasticizer, 4 phr Sb₂O₃, and stabilizer as required. For coated fabrics such as awnings, tarpaulins, inflatable structures: 100 phr PVC, 40 phr ATH, 45 phr phosphate plasticizer, 18 phr dioctyl phthalate, and stabilizer as required.

A major challenge is to incorporate enough ATH to achieve the desired flame retardancy while retaining useful flow properties and mechanical properties (especially flexibility). Plasticized PVC is rather "forgiving" and ground ATH can be used as well as the precipitated grades. However, the selection of ATH is more demanding in rigid and semi-rigid formulations. A variety of particle sizes, surface treatments and particle morphologies is available. Both reprecipitated (from commodity grade ATH) and milled products are available. As a rough guide to the selection, the larger particle size range is preferred when rapid mixing and melt flow is required. The finer particle sizes are generally slower to disperse but may be found to have somewhat higher flame retardant effect, somewhat better tensile and somewhat better tear strength [14].

Fatty acid surface-treated grades such as Martinal® OL-104C and OL-107C are more dispersible, give lower viscosity and increased flexibility in PVC. Surface treatment with silanes is available also, and may provide even better mechanical properties, especially in PVC alloys such as GE's Cycovin® alloy of PVC with ABS. In highly filled PVC, where lubricity

and melt flow must be maintained, some proprietary coated ATH grades are available from Albemarle and Huber.

ATH can somewhat compromise the heat stability of rigid PVC [15]. Adjustments in stabilizer content may be necessary. ATH is not particularly detrimental in flexible PVC [16].

4.6.2 Magnesium Hydroxide and Related Magnesium Minerals

Magnesium hydroxide occurs in crude form as the natural mineral brucite, and in finely ground form, has some usage as a low cost plastics additive. However, magnesium hydroxide usually is employed as much purer synthetic products. Moderately priced grades are available from Martin Marietta as MagShield®, from Albemarle as Magnifin®, from ICL-IP as FR-20 and from Marshall Additive Technologies as the H-TEC H® series. Some varieties contain a few percent calcium hydroxide. Higher priced magnesium hydroxide with lower surface reactivity, in some cases coated surfaces, and more compact particles are available as Kisuma® grades from Kyowa (Japan). Magnesium hydroxide is often used in rigid PVC where the processing temperature exceeds the dehydration temperature of ATH (above about 200 °C). Magnesium hydroxide loses its one molar equivalent of chemically bound water in the range of 300–400 °C, converting to magnesium oxide, and absorbs 1316 J/g (somewhat above the dehydration endotherm of ATH). Processing of formulations containing magnesium hydroxide can be done at higher temperatures than with ATH, limited mainly by the dynamic stability of the PVC. Magnesium hydroxide is usually found to be more effective than ATH as a smoke suppressant, although some exceptions have been reported by Huber [13]. Because of its basicity, it also scavenges hydrochloric acid and thus makes the smoke less corrosive. Combinations of ATH and $Mg(OH)_2$ can give protection over a wider temperature range or longer time. Various workers have found a mild magnesium hydroxide-ATH flame retardancy synergism. Recent studies at Huber do not confirm this in regard to smoke suppression in plasticized PVC [13].

A new variety of magnesium hydroxide, Vertex® 100, has been recently introduced by Huber. It has enhanced flame and smoke suppressant properties, relative to other magnesium hydroxides or ATH, attributable to “unique particle characteristics” [13]. Huber [15] and Martinswerk [17] have patented technology for surface treatment of magnesium hydroxide with siloxane oligomers, providing improved smoke and flame retardancy as well as mechanical properties in various polymers.

Besides magnesium hydroxide itself, basic magnesium carbonate (hydromagnesite) or huntite (a magnesium calcium carbonate) or blends thereof, have been used for many years as smoke suppressants in flexible PVC, typically at 5–20 % in combination with alkyl diphenyl phosphate plasticizers [18, 19]. Basic magnesium carbonate is usually somewhat hygroscopic and needs to be kept dry to avoid porosity in the compounded vinyl.

Ultracarb® (Minelco) or Marshall Additive Technologies' HM-C9 is a natural mineral, which is a mixture of huntite, $Mg_3Ca(CO_3)_4$ and hydromagnesite, $Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$. In an extensive optimization study, Ultracarb® was shown to be effective in formulating low smoke antimony oxide-free vinyl formulations containing phosphate and brominated phthalate plasticizers. It was also found that blends of Ultracarb® with calcium carbonate could be used to obtain flame retardant plasticized formulations with low acid fume release [18].

Ongard® 2 (Chemtura) has been used as an effective smoke and flame suppressant, particularly in combination with alkyl diphenyl phosphates in flexible PVC. An example of the high flame retardant effectiveness of Ongard® 2 at 2 phr in combination with antimony oxide at 2 phr in rigid PVC pipe was shown by Morley in the Wickson formulation handbook [20]. A less abrasive version, Ongard® 5, has recently been introduced.

Some interesting essentially plasticizer-free formulations of PVC with an ethylene-octene copolymer, chlorinated polyethylene (Dow's Tyrin®), compatibilized by polycaprolactone, and a high loading of magnesium hydroxide to achieve flame retardancy, have recently been described by Teknor Apex [21].

4.6.3 Molybdenum Compounds

Molybdenum compounds are regarded as the standard additives for low smoke formulations, the leading additive being ammonium octamolybdate (AOM) for vinyl applications. Studies have shown that molybdates work in the solid phase as most of the molybdenum is found in the char residue. Molybdates are said to reduce smoke by catalyzing the formation of trans-olefin structures from cis-olefin structures in the dehydrochlorinated polymer residue, so that the propensity to cyclize to soot-forming aromatic species is lessened [22].

Zinc and calcium molybdates are also effective and are available from Sherwin Williams as Kemgard®. Kemgard® 911C, a zinc molybdate on talc, is useful as a smoke suppressant, as shown in a PVC-chlorinated polyethylene wire insulation formulation [23]. Kemgard® 981 is zinc phosphate-zinc oxide, the only non-molybdenum product in the family, described as a smoke suppressant and flame retardant [24]. Newer members of this family are Kemgard® MZM, a zinc molybdate-magnesium hydroxide complex which gives good smoke suppression with good dynamic stability in rigid PVC, and Kemgard® HPSS, a basic zinc molybdate/magnesium hydroxide complex which gives good smoke suppression at low levels and flame retardancy with early char and late burnoff, also with good dynamic stability in flexible PVC [25, 26]. Favorable smoke comparisons of these products to ammonium octamolybdate have been published [26, 27]. Combinations of a molybdenum smoke suppressant with various plasticizers and stabilizers have been studied in a statistical design mode in a plenum jacket formulations; the molybdenum has some destabilizing effect, whereas increasing the phthalate plasticizer and the addition of hydrotalcite (magnesium aluminum carbonate) have stabilizing effects [28]. It is evident that the optimization of smoke and the other required properties requires systematic experimentation [26, 28].

Various proprietary combinations of AOM with zinc oxide and/or magnesium hydroxide and other smoke-reducing inorganic components are available as the LS series from Marshall Additive Technologies, previously under the Charmax trade name, now under the C-TEC trade name. Such combinations can improve smoke results and/or reduce formulation cost, which is now aggravated by the greatly increased price of molybdenum compounds [7].

Physical mixtures of molybdenum trioxide with other metal oxides (copper, iron and tin) are also reported to provide low smoke characteristics, although there is a color problem with such mixtures. Molybdenum oxide, copper oxides and ferric oxide also decrease rate of heat release and increase char [29] but only molybdenum oxide seems to have a retarding effect on dehydrochlorination [30]. It has also been hypothesized that some of the smoke

suppressant action of molybdenum may be in the vapor phase, resulting from formation of a volatile molybdenum carbonyl.

Melamine octamolybdate has been used for many years as a smoke suppressant alternative to ammonium octamolybdate. It is believed to provide better electrical properties under hot wet conditions. For improved cost/performance, it can be formulated on a high surface area mineral carrier as shown by Sherwin-Williams [31].

4.6.4 Copper Compounds

Copper salts, particularly copper oxalate in combination with a molybdate, have been used as smoke suppressants, originally under a B.F. Goodrich patent [32]. In a later series of studies by Starnes *et al.* [33], the lengthening of ignition time and the reduction of mass loss rate under cone calorimetry conditions has been recognized in addition to the smoke suppression, and insight into the modes of action of copper compounds has been gained. Reductive dechlorination with carbon-to-carbon coupling is an important feature of this action. Copper compounds also help the thermal stability of PVC compounds.

4.6.5 Zinc Borates; Barium Borate

These additives are well established in PVC as partial replacement for antimony oxide with the distinct advantage of relatively lower smoke, and anti-afterglow action. The most widely used zinc borate is $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ available as Firebrake® ZB (Rio Tinto Minerals, formerly US Borax and Luzenac) and as Marshall Additive Technologies C-TEC® CT ZB400. This zinc borate loses its 14 % water of hydration in the range of 300–450 °C. Several particle size ranges of the same compound are available, for example a particularly finely divided version Firebrake® ZBXF. Other zinc borates which are on the market and said to be useful in PVC (higher activity claimed due to higher ZnO ratio) are $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $2\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Chemtura's ZB223; Marshall's C-TEC CT ZB200). The latter is also known as zinc metaborate. These higher ZnO/B₂O₃ compounds are probably more useful in flexible PVC. A more stable hydrate, $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, Rio Tinto's Firebrake® 415 which loses its water starting at about 415 °C, and an anhydrous zinc borate, Firebrake® 500, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3$, are available but are mainly of interest for use in engineering thermoplastics. The sometimes-observed destabilizing effect of zinc borates in PVC can be related to the ZnO content; the lower the ZnO, especially any unbound ZnO component, the better. The problem is less serious in flexible PVC. Elevating the stabilizer level will also help, as will the avoidance of the more finely divided zinc borates. The action of all of these zinc borates is generally believed to be promotion of crosslinking and charring, plus formation of low melting glass which together with other inorganic fillers can form a barrier. There is also an endothermic and fuel dilution effect as the water of hydration is lost from the zinc borate hydrates. Most of the boron and zinc content remains in the char, but there may be a small vapor phase contribution for instance from volatilized zinc chloride.

Additionally, zinc borate can suppress glowing combustion (smoldering) because it alters the surface morphology of the char. Boron is known to be an inhibitor of carbon combustion, according to one hypothesis, by occupying certain active sites on the graphite lattice, whereas

other sites are inhibited by phosphorus [34]. By itself, zinc borate is a less effective flame retardant in PVC than antimony oxide, but their combinations are very effective. Depending on the fire standard to be achieved and other additives used, it is possible to replace antimony oxide in part or entirely by zinc borate, often with reduction in formulation cost and with substantial benefits in smoke reduction. Also, zinc borates show synergistic flame retardant effects with antimony oxide, especially in formulations which also include alumina trihydrate (ATH), magnesium hydroxide or calcium carbonate [4]. Synergism or at least beneficial additive effects are also seen in smoke reduction with typical smoke-lowering additives such as zinc stannates, ammonium octamolybdate or alkyl diphenyl phosphates.

A barium borate is on the market as Buckman's Flameblok®, and is said to have some advantages in afterglow suppression and low water solubility. Calcium borates, which can be quite inexpensive since they can be made by precipitation from borate-rich brine (California), are sometimes claimed to be useful (mainly in roofing) but supporting data on this is scarce.

4.6.6 Zinc Stannates

Zinc stannate (ZnSnO_3) and zinc hydroxystannate ($\text{ZnSn}(\text{OH})_6$) are colorless water-insoluble salts that are effective smoke suppressants and flame retardant synergists (they are available from Marshall Additive Technologies as C-TEC CT-ZST and CT-ZHS respectively). Economics has tended to retard the usage of these compounds. Zinc hydroxystannate is effective as both a flame retardant and smoke suppressant in PVC at about 3 phr and does not impair color or stability [15, 35]. Zinc stannate was comparable on smoke suppressant but not as effective on flame retardancy. It was found by Alcan investigators that a mixture of zinc stannate and zinc hydroxystannate was more effective than either one alone as a smoke suppressant [36, 37]. These compounds have mainly, but not exclusively, condensed phase action as "Lewis acids" [38].

As partial or even complete replacements for antimony oxide, the stannates are claimed to afford good flame retardancy (probably by vapor phase action as well as condensed phase action) with reduced smoke and carbon monoxide production [39–41]. Very good overall flame and smoke performance was obtained by an optimized combination of dodecyl diphenyl phosphate, a brominated aromatic ester (probably dioctyl tetrabromophthalate), ATH, zinc stannate, ammonium octamolybdate and antimony oxide [41]. Good smoke results were also described with zinc stannate-ammonium octamolybdate combinations by Alcan investigators [36]. Zinc stannates may allow reducing or eliminating the ammonium octamolybdate which is now (2006) more costly.

Tin dioxide coated on calcium carbonate has recently been shown by Chinese workers to be an effective smoke suppressant additive for semirigid PVC [42]. Merely adding the two materials separately did not show the same benefit.

4.6.7 Zinc Sulfide

This is a very inexpensive white pigment which has smoke suppressant retardant action in PVC. Used by itself, it is not notably flame retardant but it can replace up to about half the antimony oxide in a vinyl formulation with retention of flame retardant properties [43]. Zinc

sulfide is also available in combination with barium sulfate as “lithopone” which has been used for many years as an inexpensive white substitute for titanium dioxide.

4.6.8 Calcium Carbonate

Calcium carbonate is usually viewed as a filler rather than as a flame retardant. Although when heated to 1150 °C, it yields CO₂ endothermically, this action occurs at much too high a temperature to help retard the burning of the polymer, but calcium carbonate does act as a non-flammable diluent. During burning, calcium carbonate (especially the precipitated grades which have more surface than the ground grades) also can capture hydrogen chloride and thus can reduce the corrosivity of the smoke, as well as providing some stabilizing action. This important method for decreasing the hydrogen chloride emissions depends on the fine state of division of the calcium carbonate, and its adequate dispersion. Stearic acid surface-treated calcium carbonate, which disperses more easily, is available from a number of suppliers.

Recent reports from Huber indicate that calcium carbonate-ATH combinations may have a favorable balance of cost and flame retardant/smoke suppressant performance [13].

4.6.9 Smoke Suppressants – General Comments

Often the effort to lower smoke generation seems counterproductive to flame resistance, as they can have competing mechanisms. Some flame retardants can interfere in the combustion efficacy of the volatile species and cause more airborne soot particles to be formed. Low smoke additives can produce more combustible organic gases which burn more cleanly but can result in higher heats of combustion and thus negatively affect flame retardancy. Obviously, the balancing act of low smoke and high flame retardancy can be difficult to achieve. Formulation studies to reduce smoke and flammability have been discussed by Innes [44] who emphasizes the importance of the interactions. In general, it can be said that a significant decrease in flame spread or heat release is almost certain to lead to a decrease in total smoke release; i. e. keeping a material from burning is a good strategy for reducing total smoke.

4.7 Low Flammability Plasticizers: Phosphate Esters

In flexible vinyl compounds, the greatest source of fuel is the plasticizer. Non-FR plasticizers such as polymeric and/or co-polymer systems can contribute to the composite's ductility. These alternatives can alter the combustion mechanisms discussed previously by contributing less fuel than other plasticizers. As mentioned above, a tetrabromophthalate ester can be used as a flame retardant plasticizer, especially where low smoke and a high degree of fire retardance is required (railway cables, for instance). However, the most common approach is to use organophosphate esters as only part of the plasticizer system, in view of their higher cost and lower plasticizing efficiency. The organophosphates are much less combustible than the phthalates. They have much lower heats of combustion and tend to be moderate retardants of the flame chemistry. The phosphates, most commonly blended with dialkyl phthalates, are used in films, cables, conveyer belts, v-belts and coated textiles such as tarpaulins.

This application of organophosphates has been known since the advent of PVC as a commercial product in the 1930s. The earliest version was tricresyl phosphate made from mixed o,m,p-cresol. It was discovered in the 1930–1940 period that the ortho-cresyl isomer made tricresyl phosphates rather strongly neurotoxic, so thereafter, only m,p-cresol was used to make these phosphates. The chemistry of the toxic effect has been well understood to involve the ability of the ortho-cresyl phosphate structure to be bio-oxidized to a cyclic phosphate which can attack an esterase enzyme, although the p-ethylphenyl group also shows a related toxic effect by a slightly different mechanism [45].

4.7.1 Triaryl Phosphates

The cresyl diphenyl phosphate is used more often in Europe and Asia because of its efficiency and low cost. For most US markets, however, it is less often used because of volatility and toxicity concerns [46], although if free of o-cresyl isomer, it is not a serious neurotoxicant. Triaryl phosphates in the US based on “natural cresylics” are likely to be tricresyl phosphate. Trixylenyl phosphates have been used where high temperature performance is important or long term heat resistance such as in agricultural (greenhouse) film, or in automobile seating where avoidance of windshield fogging is required.

Tricresyl phosphate replacements have evolved by substituting the cresol (which has become increasingly costly) by a synthetic isopropylphenol-phenol mixture to produce a mixed triaryl phosphate, most commonly approximating diphenyl isopropylphenyl phosphate. This development was originally driven by the erratic supply and pricing due to the by-product nature of the cresols (the original coal tar source dwindled, leaving only a petroleum byproduct source). Although one study showed the ortho-isopropylphenyl isomer to be the best from a stability standpoint [47], the commercial products appear to be a mixture of isomers. The isopropylphenyl phenyl phosphates with lower and higher levels of isopropyl substitution have been sold as flame retardant PVC plasticizers, such as Akzo Nobel's (now ICL-IP's) Phosflex® 21P, 31P and 41P or FMC's Kronitex® 50 (similar to cresyl diphenyl phosphate in physical properties and Kronitex® 100 (similar to tricresyl phosphate in physical properties). FMC triaryl phosphate products are now made and sold by Great Lakes Chemical (now Chemtura) as Reofos® 50, 65 and 95 (from isopropylphenols) and Pliobrak® CDP, TCP and TXP (from cresols and xylenols). Certain products of the Bayer (Lanxess) Disflammol® family are of this type.

According to an FMC author [48], a typical isopropylphenyl phosphate consists of 7–30 % triphenyl phosphate, 10–20 % 2-isopropylphenyl diphenyl phosphate, 2–3 % 3-isopropylphenyl diphenyl phosphate, 10–15 % 4-isopropylphenyl diphenyl phosphate, 7–19 % di(2-isopropylphenyl) phenyl phosphate, and 25–63 % higher alkylated triaryl phosphates. This author also points out that the isopropylated triphenyl phosphates are unique compared to tricresyl phosphates in that they have conveniently high plastisol fusion rates, but somewhat slower than tricresyl phosphates. In coating fabric, this property is advantageous in allowing more time for effective coating and penetration. They also have smaller increases in viscosity in storage, thus better storage stability of the plastisol [49].

A related product is tertiary-butylphenyl diphenyl phosphate made from tertiary-butylphenol produced from phenol and isobutylene. This was originally introduced in the 1970s as a

functional fluid (hydraulic applications) but has also been found useful in PVC. It is available from Akzo Nobel (now from Supresta) as Phosflex® 61B and 71B. By itself, it has inferior plasticizing activity compared to the isopropylphenyl homolog, but when diluted with a phthalate plasticizer, its activity is adequate, and it has some advantages of thermooxidative stability [50]. It has good flame retardant activity and imparts rapid gelation characteristics to PVC plastisol formulations as well as good resistance to microbial damage.

The triaryl phosphates are more costly and somewhat less effective as plasticizers than the common dialkyl phthalate plasticizers. Plasticized PVC usually is under price constraints, so compounders of plasticized PVC will typically use mostly the dialkyl phthalate, mixed with no more of the triaryl phosphate than is needed to comfortably pass whatever flammability requirements must be met. In general, the more highly plasticized the formulation, the higher the ratio of phosphate to phthalate to meet a given flame retardancy; in an unfilled plastisol system with 80 parts of plasticizer per 100 parts of resin, 25 % of the triaryl phosphate in the plasticizer mix (20 phr) is suggested as a minimum.

Table 4.3 Comparison of PVC with Various Phosphate Plasticizers

Identity of phosphate	Viscosity mm/s 25 °C	Density at 25 °C, g/cc	Shore A hardness	Cold flex Clash & Berg °C	Oxygen index (%)
Isopropylated phenyl	44.5	1.183	74	−2	32.6
Isopropylated phenyl	48	1.174	75	−2	32.5
Isopropylated phenyl	57	1.164	76	−1	32.5
Isopropylated phenyl	93	1.136	78	+1	32
Cresyl diphenyl	36	1.202	73	−4	33
Tricresyl	60	1.158	74	0	32.5
Trixylenyl	95	1.134	76	+4	32
t-Butylphenyl diphenyl	81	1.165	89	+11	32
2-Ethylhexyl diphenyl	16	1.087	70	−24	28.6
Isodecyl diphenyl	22	1.065	71	−20	28.1
For comparison:					
Diocetyl phthalate	56	0.980	71	−24	24
Diisononyl phthalate	85	0.970	75	−19	24
Tetrabromo-phthalate	1036	1.54	94	+18	37.5

4.7.2 Low Temperature Alkyl Diphenyl Phosphate Plasticizers

The triaryl phosphates impart undesirable stiffness to plasticized PVC at low temperatures. In the 1950s, Monsanto developed 2-ethylhexyl diphenyl phosphate (now Santicizer® 141) and isodecyl diphenyl phosphate (Santicizer® 148). Along with Santicizer® 2148, apparently a variant of Santicizer® 148, with even lower smoke and better low-temperature plasticizing properties, these are now available from Ferro Corp. Products similar to Santicizer® 141 and 148 were later available from Akzo Nobel (now ICL-IP) as Phosflex® 362 and 390, respectively. Octyl (probably 2-ethylhexyl) diphenyl phosphate has been available from Bayer (now Lanxess) as Disflammol® DPO. These partially aliphatic phosphates are more plasticizing than the triaryl phosphates. Uses are in tarpaulins, automobile seating, flooring, conveyer belts, and cable sheathing, especially plenum cable jacketing. They also are said to have advantages in weathering, gelling properties, and resistance to saponification (by alkaline detergents, for example). They are somewhat less effective than the triaryl phosphates from a flammability standpoint but distinctly better in smoke evolution [51].

A Teknor Apex patent [52] shows the use of pentaerythritol ester plasticizers (Hercoflex®) in combination with isodecyl diphenyl phosphate and a tetrabromophthalate plus ATH and Charmax® (now C-TEC®) LSZ4A in low smoke formulations for wire and cable insulation. Data in this patent shows that lowering the tetrabromophthalate and raising the ATH level is favorable to low smoke in a wire and cable insulation formulation.

4.7.3 Comparison of Some Flame-Retardant and Non-Flame-Retardant Plasticizers

Comparative data in Table 4.3 was selected from a Great Lakes Chemical (now Chemtura) bulletin "Speciality Plasticizers for PVC" for a formulation containing 100 parts of a PVC suspension polymer (viscosity 128 by ISO R174), 60 phr of the indicated plasticizer, 1 phr Irgastab® 17M and 0.2 phr Irgawax® 0.2 (Table 4.3).

4.7.4 Comparison of Various Combinations of Plasticizers and Other Additives

Some more or less advantageous combinations (from differing criteria) are shown in Table 4.4 [53]. The triaryl phosphate (TAP) is isopropylphenyl diphenyl phosphate. The data were obtained in the cone calorimeter at 50 kW/m².

These data show that the preferred formulation should depend on the criteria used, which is no surprise. Some advantage is seen by cone calorimetry in combining antimony oxide and zinc borate. The combination of the triaryl phosphate with antimony oxide, while not actually antagonistic, shows a distinctly less-than-additive effect and is thus relatively inefficient. On the basis of LOI, zinc borate appears superior to antimony oxide in combination with the triaryl phosphate. The presence of ATH produces a possibly useful slow burning effect.

Table 4.4 Comparison of PVC with Various Plasticizer/Additive Combinations (Cone Calorimetry and Other Data)

Additive(s) to PVC	Additive level (phr)	Burning time (s)	Peak heat release rate (kW/m ²)	Time to peak heat release (s)	Char (wt.%)	LOI (% O ₂)
Diisodecyl phthalate	50	128	45.1	35	6	23.5
Antimony oxide	6	134	36.8	48	12	29.8
AO/zinc borate (ZB)	6/6	144	42.1	38	22.4	30.5
Triaryl phos- phate (TAP)	50	148	40.8	46	7.7	31.8
TAP/ZB	50/6	200	30.6	54	10.8	34.7
TAP/AO	50/6	180	44.4	70	9.2	32.9
TAP/AO/ZB	50/6/6	176	23.9	34	18.3	33.3
TAP/AO/ ZB/ATH	50/6/6/30	300	25.4	52	10.5	37.1

4.8 Formulating for Specific Applications

A still-useful general reference (1993) is a handbook by Wickson [20]. A new handbook by R. Grossman was published in 2008 [2]. The following formulations are taken from recent commercial sources.

4.8.1 Calendered Vinyls

For thin film laminates, antimony oxide is frequently used in combination with other inorganic additives. Alumina trihydrate, magnesium hydroxide and zinc borate are the principal

Table 4.5 Typical Vinyl Formulation for Wall Covering

Component	phr
PVC	100
Diisodecyl phthalate	26
Phosphate ester	20
Sb ₂ O ₃	2–4
Zinc borate	5–10
ATH	10–15
CaCO ₃	40
Stearic acid	0.3
Stabilizer	3–5

choices. All of these are useful for lowering smoke. Alternatively, phosphate ester plasticizers are used, again, often with ATH and/or magnesium hydroxide. For good smoke suppression, the zinc-magnesia composition Ongard® 2 or zinc borate can be added. Also, where smoke is an important criterion, the alkyl diphenyl phosphates are often preferred instead of the triaryl phosphates.

Different applications have different requirements. Some typical or “starting point” formulations are listed below.

For wall covering, in order to pass the ASTM E-84 tunnel class 1 requirement on smoke developed index (almost all vinyls meet flame spread index requirements of 25) [54] (Table 4.5). For automobile upholstery, to meet Federal Motor Vehicle Safety Standard 302 [54] (Table 4.6).

Table 4.6 Vinyl Formulation for Automotive Upholstery

Component	phr
PVC	100
Diisodecyl phthalate	70–80
CaCO ₃	25–50
Epoxidized soybean oil	5
Stabilizer	3
Sb ₂ O ₃	1.5–2.0
Zinc borate	1.5–2.0

For wire and cable insulation to meet the UL NM cable requirements [55] (Table 4.7).

Table 4.7 Vinyl Formulation for Wire and Cable Insulation

Component	phr
PVC resin	100
Plasticizer (7-11 phthalate)	40
Mg hydroxide	30
Calcium carbonate	20
Stabilizer	3
Antimony oxide	3
Stearic acid	0.5
Properties	
LOI	31.0 %
Tensile strength	2610 psi
Tensile modulus	20330 psi
Elongation	139 %
Melt flow index	0.9 g/10 min.

A series of UL approved building wire formulations developed by Exxon-Mobil for TW (mois-
ture-resistant), THW (hot-water-resistant), and THWN/THHN (hybrid nylon conductor

insulation/PVC jacket) is given by Coaker [56]. These formulations use various combinations of calcined clay, calcium carbonate and antimony oxide with phthalate or trimellitate plasticizers. Cable jackets which must pass the more severe vertical cable tray test UL 1685 for flame spread and smoke release generally will include some ATH.

4.8.2 Plenum Wire and Cable

It is typical in the US to place communication, alarm and signalling wiring in plenums (concealed spaces which are also part of the air distribution system). If such wiring is not very fire-resistant, this practice can cause fire and smoke to spread rapidly and stealthily through a building. Extremely severe fire and smoke requirements, generally based on the NFPA 262 tunnel test, have been imposed where wire and cable are not protected by metal conduits or sprinklers. The challenge to vinyl formulators has been to reach flame and smoke levels to compete with the expensive fluoropolymer coated constructions. Some PVC formulations have been recommended for plenum use, for example the following in a 1993 patent of the Belden Division of Cooper Industries [57] (Table 4.8).

Table 4.8 PVC Formulation for Plenum Cables

Component	phr
PVC (Geon 30)	100
Santicizer® 2148 phosphate plasticizer	30
Diocetyl tetrabromophthalate	20
Epoxidized soybean oil	3
Alumina trihydrate	30
Ammonium octamolybdate	30
Zinc molybdate	10
Tribasic lead sulfate	7
Stearic acid	0.5
Paraffin wax	0.5

A formulation from Teknor Apex for low smoke PVC wire and cable shows, in place of AOM with close results, an alternative smoke suppressant, Charmax LSZ4A (now Marshall Additive Technologies C-TEC® LSZ4A) (Table 4.9) [52].

Cable constructions using this composition passed the UL 910 Steiner Tunnel test, and had OI of 46 by ASTM D-2863.

More recently, various alloys of PVC with thermoplastic elastomers have been shown to have good flame and smoke properties suitable for plenum applications [5]. These vinyl-based products are said to compete with fluorinated polymer (FEP) coatings under present codes and standards. These regulations and standards are currently in a state of flux. In some cable constructions, a PVC sheath is used over FEP insulation, preferably with a low-smoke low-flame-spread PVC formulation. In some patented compositions, a non-flame-retardant insulation, optimized for electrical properties, is surrounded by wraps and jackets of more flame retardant properties, often PTFE and low smoke PVC-based; an example is a patent by

Table 4.9 Low Smoke Wire and Cable Formulation with Less Costly Smoke Suppressant

Ingredient	Amount (by weight)
Polyvinyl chloride resin	100
Pentaerythritol ester plasticizer (Hercoflex® 707)	31
Calcium carbonate	10
Calcined clay (Engelhard SP33)	5
Alumina trihydrate (Alcoa C710B)	60
Basic lead heat stabilizer	7
Stearic acid lubricant	0.25
Antimony trioxide	5
Brominated phthalate (Chemtura DP45)	10
Long-chain alkyl diphenyl phosphate (Santicizer 2148)	5
Zn-Mo complex (Charmax LSZ4A, now C-TEC LSZ4A)	10
Zinc borate (Climax ZB467)	2

Belden [58] which describes using low smoke PVC formulations (proprietary) from Alpha-Gary and Gitto Global. Solving cable requirements by constructional means using layers with different properties is essentially outside the scope of our review.

Some polymer blend formulations making use of ATH and magnesium hydroxide-carbonate said to be suitable for plenum are presented in 1999 by S. Brown (Alcan) [59] (Table 4.10).

Table 4.10 Various Polymer Blend Formulations Suggested by Alcan for Plenum Cable

Component	A phr	B phr	C phr
PVC	100	100	100
Elvaloy® HP-441 (DuPont ethylene-acrylate-CO)	15	15	15
Dodecyl diphenyl phosphate plasticizer	10	10	10
Diocetyl tetrabromophthalate plasticizer, f.r.	25	25	25
Alumina trihydrate	40	40	40
Huntite/hydromagnesite mix	10	10	10
Hindered phenolic stabilizer (Ciba)	4	4	4
Tribasic lead sulphate stabilizer	3	3	3
Antimony trioxide f.r. synergist	3	3	3
Ammonium octamolybdate (AOM, anti-smoke)	25		10
Zinc stannate (ZS, f.r. synergist and anti-smoke)		25	15
Cone calorimetry data at 40 kW/m ²			
Time to ignition (s)	897	705	never
Peak rate of heat release (kW/m ²)	35	35	—
Average specific extinction area (m ² /kg)	433	342	—

Formulations A, B and C are said to be useful starting point formulations. These results suggest a synergism of the AOM and ZS. Chlorinated PVC has also been proposed as a useful component in plenum wiring formulations.

A more extensive discussion by Griffin (2000) of the use of the ethylene-acrylate-carbon monoxide copolymers (DuPont's Elvaloy® HP series, especially ECR-742 and ECR HP-441) presents data showing that these resin modifiers used in PVC formulations can reduce smoke without sacrifice of strength, elongation, flex modulus or brittle point [60]. Plenum cable applications are suggested.

Some remarkably complex polymer blend formulations have been developed for cable insulation and jacket by Furon Co., using a combination of PVC, chlorinated PVC, an ethylene acrylic elastomer, polycaprolactone (most likely, in the role of a compatibilizer), phosphate and trimellitate plasticizers, and several flame and smoke suppressants (Table 4.11).

Table 4.11 Plenum Wire and Cable Jacket Formulations [61]

Component	Wire insulation (parts by weight)	Jacketing (parts by weight)
Geon® 86 × 1 PVC	70	65
Temprite® 674 chlorinated CPVC	30	35
Vamac® G ethylene acrylic elastomer	20	45
Isodecyl diphenyl phosphate plasticizer	8	13.0
TiO ₂ pigment	2	5.0
Pol-U® molybdenum oxide composition	4	6.0
Micral® 932SP or CM hydrated alumina	20	110.0
H(DYT) D80 dibasic lead phthalate	12	8.0
II(TBS) D80 tribasic lead sulfate	0.30	—
Antimony trioxide	4.0	5.0
ZB223 (zinc borate; 2ZnO·2B ₂ O ₃ ·3H ₂ O)	—	8.0
Irganox® 1010 hindered phenol antioxidant	0.30	0.3
Ca stearate	1.50	0.50
Structol® TR016 lubricant	1.0	—
Jayflex® triisononyl trimellitate plasticizer	8.0	8.0
P-tone® 700 high mol. wt. caprolactone polymer	20	20.0
Zerogen® 10 SP magnesium hydroxide	20	—
Physical Properties		
Oven aging ICEA S-19-81*, 7 days/121°C	Passes 90 °C rating	Passes 90 °C rating
Tensile, retention* (%)	112 %	140 %
Elongation retention* (%)	86 %	50 %
Flammability/smoke		
LOI (O ₂ %) (ASTM D2863)	44.0	61.0
D _m smoldering (E662)	105	95.5
D _m flaming (E662)	154	103.5

This patent shows many interesting compositional variations and their effects on flammability, smoke and physical properties [61].

There has been a long-term competition in the plenum cable market between fluorocarbon elastomers and low-smoke highly flame retardant vinyls. Interestingly, Teknor Apex wire-and-cable researchers have learned how to make hybrids of plasticized PVC with fluoropolymers using acrylate compatibilizers [62]. In a review by Kroushl [63], it is mentioned that polyvinylidene fluoride-PVC blends have also been commercialized but have a cost problem.

4.8.3 Coated Textile Applications

This application of PVC in regard to flame and smoke performance has been reviewed in 2006 by a Chemtura author [64]. Flame retardant coated fabrics often have a two-layer vinyl coating, the inner layer being plasticized with a phosphate (triaryl or alkyl diphenyl) plus a phthalate ester, and sometimes a chloroparaffin secondary plasticizer. The outer layer is often plasticized with a combination of a phosphate plus a non-fugitive polymeric (oligomeric) ester plasticizer. Additional components may include antimony oxide, zinc borate or ATH. A thin acrylic topcoat may also be applied.

Decabromodiphenyl ether (usually with antimony trioxide) is also very cost/effective as a component of flexible PVC textile backcoatings. Its blooming tendency, light stability shortcomings and environmental concerns are limiting its use. Other polybrominated additives discussed above also find some use in this area.

Roofing webs consisting of fabric coated on both sides with plasticized PVC, where the plasticizers must be selected for non-volatility and compatibility with bituminous roofing materials, are flame retarded with antimony oxide.

4.8.4 Vinyl Flooring

Vinyl sheet flooring usually has two vinyl layers on a fibrous backing, the lower layer being plasticized usually with a phosphate (triaryl or alkyl diphenyl) plus butyl benzyl phthalate. The top (wear layer) usually has a low level of flammable plasticizer so that it does not need a flame retardant phosphate. Vinyl tile flooring usually does not need a flame retardant because of the usually high filler level (calcium carbonate and/or clay) and low level of plasticizer (such as butyl benzyl phthalate). An acrylic or urethane topcoat is sometimes used but may be somewhat adverse to flame retardancy.

4.9 PVC from a Safety and Environmental Point of View

Misleadingly, PVC has been accused of producing particularly toxic smoke. It is quite well established that carbon monoxide is the main killer, and that the toxicity of fire atmospheres is determined almost exclusively by carbon monoxide. The smoke toxic potency of HCl is of the same order as that of carbon monoxide. Moreover, hydrogen chloride is rather unique amongst major combustion products in that its concentration decays in a fire as it reacts or is absorbed by many surfaces. In room corner tests (Factory Mutual), the obscuration caused

by PVC was less than comparative wood panels. A summary of these relationships has been published by Hirschler [5].

PVC, in common with other halogenated materials, has been under environmental attack for decades. The objections to PVC and other halogenated products are summarized at great length by an author connected to Greenpeace, an environmental activist organization [65]. The production of PVC is alleged to release toxic by-products. The stability of PVC to biodegradation, while a virtue for a building material (in common with concrete, stone, brick, metal and glass), does pose a disposal question. Recycling is certainly possible and is done to some extent [66]. Landfill disposal is possible in the United States, where there is ample landfill capacity but is less acceptable in Europe or Japan, where there are fewer suitable areas. Incineration has been controversial because of the formation of polychlorinated dibenzodioxins and -dibenzofurans. There is a very large body of toxicological literature on these paradoxical compounds, certain isomers of which are extraordinarily toxic to some animal species, although the only acute toxic symptom upon high exposure in humans is a skin eruption called "chloracne." However, incineration in modern government-permitted incinerator-scrubber installations has been found to produce little or no dioxins [67]. Disposal by burning in smelters and cement kilns is also an option, if it is adequately monitored.

Since PVC has favorable properties from an ignitability, flame spread and ease of extinguishment point of view, it must be recognized that PVC is less likely to be a contributor to fire than many other plastics. Less well known is the fact that the heat release characteristics of unplasticized PVC are one of the lowest of all combustible materials [5, 44]. Of course, the addition of a conventional phthalate plasticizer will raise the peak rate of heat release, but as discussed above, much less flammable plasticizers are used where fire behavior is important.

Few plastics have had as thorough a study of environmental impact, and increasingly production and use of PVC can be shown to be surprisingly benign from a resource and sustainability standpoint [68]. German cities which banned its use in construction have for the most part returned to its use. Green organizations continue to agitate against PVC and halogenated products in general, largely based on obsolete information regarding incineration and emissions, but the industry has had some success in educating the public and government regarding the safety of PVC. The objectionable cadmium stabilizers have been phased out, and lead stabilizers which have caused some concern are being gradually replaced. Alternative plasticizers have been defined to replace the often-criticized dioctyl phthalate in sensitive applications.

Frequently updated data resources in support of PVC are available on the Internet [66, 68]. PVC in wire and cable has held its position vs. non-halogen alternatives except in situations where smoke and combustion product corrosivity are dominant considerations, or where "green" marketing strategies prevail. Large new manufacturing facilities for PVC in the U.S. are being planned and built [69]. New PVC facilities are also being built or planned in Europe and Asia [70–72]. Efforts are being made by the vinyl industry, particularly in Europe where the challenge is most intense, to lower the usage of lead-based stabilizers and to develop better means for recycling of PVC [73]. These incompletely solved problems have not prevented growth in the usage of PVC [74]. A leading producer claims that global vinyl growth is 6 % per yr. and in Eastern Europe and Asia, 15 % per yr. [75].

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5 Current Practice and Recent Commercial Developments in Flame Retardancy of Polyamides

5.1 Introduction

Thermoplastic polyamides have applications in electrical, electronic, automotive and other industrial resin applications, and also in textiles which will be discussed (with some overlap) in a separate chapter. Many of the applications require flame retardancy. Reviews of the thermal decomposition of polyamides, their fire properties and flame retardant technologies has been published by the present authors, covering the literature and patents subsequent to 1970 [1, 2]. Those reviews were not limited to actual commercial practice, in contrast to our intention in this chapter to focus on commercial or near-commercial systems, and to provide a useful guide to the compounder. Where no reference is cited in the chapter, the source is the manufacturers' product literature. A brief but quite informative overview from a commercial standpoint was published elsewhere [3]. A review from EMS-Grivory [4] discusses a wide range of polyamides which can be tailored for demanding flame resistant cable applications including optical cables; critical factors include flexibility, processing ease, and strippability in the case of optical cables.

A table of 2003 European flame retardant tonnages in the automotive and electrical/electronic applications for flame retardant reinforced and unreinforced polyamides was presented by a German research group in 2005 [5].

The principal polyamides requiring flame retardancy are polyamide 6, polyamide 66, also "high temperature polyamides" such as polyamide 4,6 (DSM's Stanyl®), Solvay's Amodel® and DuPont's Zytel® HTN. The high temperature polyamides typically have an aliphatic diamine reacted with an acid which is usually at least partly terephthalic or isophthalic [6]. Polyamides, which are totally aromatic structures (aramides), tend to be inherently flame retardant, but polyamides with aliphatic components are inherently flammable. Since they crack to volatile fuel (or in the case of polyamide 6, depolymerize to cyclic monomer) and do not form much char, and moreover, are rather sensitive to property loss caused by additives, they are challenging polymers to flame-retard [1]. On the other hand, polyamides tend to be slow-burning compared to the hydrocarbon plastics. Polyamide 66 has an oxygen index of about 28, compared to 17.4 for polyethylene. The low viscosity of the melt and loss of heat from the burning material resulting from melt flow tends to raise their apparent flame resistance. Interestingly, unfilled polyamide 6,6 can give two values of oxygen index: about 21 if it burns in non-dripping mode and about 28 if it burns in the melt flow-dripping mode [7]. Unmodified polyamides are often rated V-2 by UL 94, although with glass fibers present (which interfere with mass flow, and act as a wick) they rate lower, usually HB by UL 94 and less than 22 by oxygen index.

Probably the largest uses for flame retarded polyamides is in electrical parts, such as wire jackets, cable straps, connectors, switches, relay housings, coil bobbins and other telecommunications and computer parts. Other electrical uses are in power tool housings, and wall plates. The UL 94 test is most commonly the basis for flammability assessment in the US, and target ratings are V-0 (< 5 second extinguishment, no flaming drip) or sometimes V-2 (< 30 second extinguishment, flaming drip allowed).

The glow wire test (UL 746C/IEC 60695-2) is also required in some cases and European standards often make use of this sort of hot wire ignition test. Requirements for many household applications require a glow wire ignition temperature by IEC 60695-2-12 or 13 of greater than 750 °C.

In some applications, polyamide electrical parts may be exposed to current leakage across their surface, and as a result, the Comparative Tracking Index (CTI) is also measured (UL-746A/IEC 60112). In this test, salt solution is applied at increasing voltage until a conductive track appears.

A comprehensive discussion of worldwide fire test methods is available in the book by Troitzsch [8].

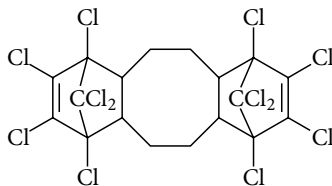
Automotive uses for polyamides are large but usually electrical connectors in automobiles do not require flame retardants except in some European under-the-hood applications. An auto industry move to higher voltage electrical systems will probably require more flame retardant materials such as polyamide connectors. Most electronic components mounted under the hood are regulated as electrical and electronic devices and require a UL-94 V-0 rating. In the electrical/electronic area, the trend is to smaller, thinner-walled but stronger and more dimensionally stable products.

The aramide textiles, notably m-phenylene isophthalamide (DuPont's Nomex®) and especially p-phenylene terephthalamide, have inherent flame retardant properties deriving from their high char yield. Nomex is occasionally enhanced by special finishes for extremely demanding fire-retardant applications, such as certain military applications. The textile applications of these fibers are further discussed in our later chapter on Textiles.

5.2 Additives for Polyamide 6 and 66 in Engineering Thermoplastic Applications

5.2.1 Chlorinated Additives

Halogen compounds have long been used, usually with a synergist such as antimony trioxide. One of the earliest successful additives, still used, is Oxychem's Dechlorane Plus®. It is a stable polycyclic polychlorinated compound made by the Diels-Alder addition reaction of hexachlorocyclopentadiene with cyclooctadiene-1,5 (a butadiene dimer).



The chlorine atoms resist hydrolysis and dehydrochlorination; the molecule is high melting and stable enough to be processed up to about 300 °C. Advantages are: less discoloration, non-blooming (compared to decabromodiphenyl ether), higher CTI possible, lower smoke and possibility for avoidance of antimony oxide.

The usual addition level in non-reinforced polyamide 6 is in the range of 20–25 % plus about 5–10 % antimony oxide as synergist. Similar or slightly lower levels are used in non-reinforced polyamide 66. Somewhat higher levels are used, typically 25–35 % Dechlorane Plus in glass-reinforced polyamide 6 or 66. In reinforced polyamide 66, no antimony oxide is necessary, and in reinforced polyamide 6, about 2 % antimony oxide is used [9]. A detailed mechanism of synergism between Dechlorane Plus and Sb_2O_3 in polyamide 6.6 was published by Starnes [10]. If extremely low smoke is needed, it is advantageous to use other metal oxides, in particular red iron oxide [11]. Combinations of Dechlorane Plus with various other metal oxides, insoluble salts and polybrominated additives are reported to have various advantages, including lower loadings and improved stability [12]. If comparative tracking index (CTI) is important, the use of zinc borate, zinc oxide, or a zinc stannate/zinc borate mixture is helpful [13, 14].

Table 5.1 Some Representative Formulations in Polyamide 66 [15]

Component (%):							
Polyamide 66	70	70	70	82	78	70	85
Dechlorane Plus	20	20	20	14	16	20	12
Antimony trioxide	10				2		
Zinc borate		10			4	5	1.5
Zinc oxide			10			5	
Ferric oxide				4			1.5
UL 94 Results:							
At 1.6 mm	V-0	V-0	V-0	V-0	V-0	V-0	V-0
At 0.4 mm	V-0	V-0	NC	V-0	V-0	V-0	V-0
CTI (volts)	275	300	600	275	425	375	350

Combinations of Dechlorane Plus with zinc borate in polyamides have smoke and UV stability advantages [16]. However, thermal stability limitations result in most of this Dechlorane Plus system being used in unreinforced polyamides, less frequently in glass-reinforced polyamide 6 and 66/6 blends, and still less frequently in polyamide 66.

Improved CTI in polyamide 66 (up to 500 v.), improved thermal stability and reduced mold corrosion can be achieved by using 2 % zinc molybdate on talc (Sherwin-Williams' Kemgard® 911C) in place of antimony oxide, with 16 % Dechlorane Plus.

5.2.2 Brominated Additives

5.2.2.1 Decabromodiphenyl Oxide and Other Polybrominated Diphenyl Oxides

One of the most efficient (and probably most cost-efficient) flame retardant additives is decabromodiphenyl oxide (decabromodiphenyl ether). It is very high melting and insoluble in the polymer, acts as a filler and has negative effects on impact, flexibility and flow. There is also some tendency to darken under UV exposure. A typical loading to reach V-0 in polyamide 6 uses about 14 % bromine in the form of decabromodiphenyl ether with about 6–7 % antimony oxide and a small amount (1 % or less) of powdered polytetrafluoroethylene (PTFE) to retard dripping. Decabromodiphenyl ether is not as satisfactory in polyamide 6,6 because of slight blooming and some discoloration.

Decabromodiphenyl oxide has been used as a textile flame retardant, particularly by back-coating with a binder and usually with antimony oxide as synergist; this system performs well other than aesthetic effects, on polyamide fabrics as well as on most other fabrics. Recent improvements involve Israeli work on reducing the particle size to 90 % below 500 nm and 10 % below 90 nm, which provides better adherence to the fabric with low amounts of binder, and better textural properties [17].

A larger molecular weight member of the brominated phenyl ether type is tetradecabromodiphenyloxybenzene, Albemarle's Saytex® 120, which has significant advantages where high temperature processing is done. It melts above the processing temperature of polyamide 6,6, has good non-blooming and rather good light stability properties. It is therefore a preferred additive in unreinforced polyamide 6,6. A typical use level is about 13 % Saytex 120 and about 5 % antimony oxide.

The entire family of polybrominated diphenyl ethers has come under environmental criticism, largely the result of pentabromodiphenyl ether being found widely distributed in fatty tissues of live organisms. On the other hand decabromodiphenyl ether, because of negligible vapor pressure and insolubility, was not found only as a pollutant close to the production sites and polymer compounding facilities. Release control measures were suggested by the EU commission and the industry has developed and is implementing a Voluntary Emissions Control Action Program (VECAP) [18].

5.2.2.2 Bromoaromatic Alternatives to Brominated Diphenyl Ethers

Marketing and public image pressures have generated interest in non-oxygen-containing substitutes for brominated diphenyl ethers. One such substitute is Albemarle's Saytex® 8010 or Chemtura's Firemaster® 2100, both of which are decabromodiphenylethane. This solid additive has similar efficacy, good thermal stability, and better UV stability than decabromodiphenyl ether, but somewhat more costly. It is mainly used in unreinforced applications.

Typical use levels in unreinforced polyamide 6,6 are 14 % of the brominated additive and 5 % antimony oxide [19] or 18 wt. % of the brominated additive and 5 % sodium antimonate [20]. In a Mitsubishi Engineering Plastics patent application [21], decabromodiphenylethane at levels of 13 parts with 68 parts of a polyamide 6 (mixture of two molecular weights), 32 parts of polyamide 66, 13 parts of melamine cyanurate and 1.9 parts of zinc borate (no antimony oxide) is shown to afford a V-2 rating with glow wire ignition temperature (GWIT) of 850 °C and comparative tracking index of 425 V. Interestingly, higher levels of the flame retardants to reach V-0 gave lower GWIT, below 800 °C.

5.2.2.3 *Polymeric Dibromophenylene Oxide*

Great Lakes' PO64P was introduced in the early 1980s as a melt blendable oligomer useful in polyamide 6 and blends of 6 and 66. The oligomers were made by oxidative polymerization of tribromophenol [22]. Two varieties were available, one with tribromophenoxy end groups and the other with phenoxy end groups (for patent reasons). They provided higher thermal stability than Dechlorane Plus. Because later substitutes were more economical, these may have been withdrawn. Similar material is still probably available in Japan [23].

5.2.2.4 *Brominated Polystyrenes as Flame Retardant Additives*

There are two families of these, differing in their mode of manufacture [24]. The older family is made by post-bromination of low molecular weight polystyrene. This reaction proceeds mostly by ring substitution of hydrogen by bromine on the benzene ring but some side reactions (probably aliphatic backbone substitution) introduce a small amount of labile halogen which reduces the thermal stability. Processes have been developed to remove this labile halogen and/or to stabilize the product against decomposition of the labile structures, but there is still a level of impurities which reduces the thermal stability. The earliest introduction of these products was Pyrochek® 68PB (Ferro, now Albemarle). It is used in both polyamide 6 and 66, on a large scale in the latter. It is also available from ICL-IP as FR-803P [25].

However, the thermal instability of Pyrochek 68PB at about 340 °C compounding temperature limits its use in some reinforced polyamide applications, and in those cases, Albemarle's HP-7010, a purer brominated polystyrene with about 2.7 bromine atoms on each phenyl group and a molecular weight of about 600 000, is preferred since it is adequately stable to about 360 °C compounding temperature. Recent disclosures from Albemarle show a new bromostyrene polymer HP-3010 with improved melt flow and thermal stability properties [26]. Saytex HP-3010 may correspond to a product made by catalyzed bromination of anionically polymerized styrene as described in an Albemarle patent which deals mainly with pelletizing the product [27]. Saytex HP-3010 and also HP-7010 provide V-0 ratings at 0.8 mm at 20.7 % loading (14.2 % Br) and 6.2 % Sb₂O₃ with 0.4 % PTFE or 22 % HP-3010 plus 10 % zinc borate plus 0.4 % PTFE [28]. Both formulations can be recycled well, with HP-3010 somewhat better, with good retention of useful properties and without mold deposit or corrosion problems. A comparison of HP-3010 and PB 620, another available brominated polystyrene, has been published by Albemarle [29].

The other family of brominated polystyrenes is made by polymerizing preformed dibromostyrene or mixed di-/tribromostyrene. In this way, a family of products can be made differing in bromine content and molecular weight. Copolymers with 0.5–2 % of comonomers are also made. This family of products is on the whole more thermally stable than the post-brominated polystyrenes. By adjustment of molecular weight, melt blendable additives are made, and strength properties and flow characteristics can be optimized.

The homopolymer of dibromostyrene with 59–60 % Br is Great Lakes' (Chemtura's) PDBS-80. This additive is well established for use in high temperature polyamides, and can be safely processed at about 360 °C. It also helps melt flow, and has good color, both initial and aged. Subsequently, a 64–65 % Br product was developed (PBS-64) by copolymerization of di- and tribromostyrene to obtain Mw 28 000, which is effective at slightly lower loading than PDBS-80. By molecular weight control, good flow properties were also obtained. A higher molecular weight (60 000) product, PBS-64HW has lower flow, but better tensile and impact properties in the resultant polyamide. It is quite suitable for use in polyamides 6 and 66.

A typical UL 94 V-0 formulation in a 30 % glass filled polyamide uses about 22 parts of PDBS-80 and 7 parts of antimony trioxide. The thermal stability is good up to 330–340 °C where the post-brominated polystyrene product is causing some degradation. Recent patents to DuPont show improved thermal stability of PDBS-80 when it is used in combination with acid scavengers such as hydrotalcite [30], calcium oxide or calcium carbonate [31].

Typically, all of these bromine-containing polystyrenes are not fully miscible with the polyamide and they form a separate phase. It was found that a copolymer, such as Great Lakes' CP-44B, with 1 % or less of glycidyl methacrylate gives much better compatibility [32]. These copolymers can react with the end groups of the polyamide. They provide a drip suppressant effect so that the usual drip suppressant (such as PTFE) can be eliminated or reduced. It may be possible to reduce the level of antimony oxide also, offsetting the somewhat higher cost of the copolymer. CP-44B appears to be a good balance of properties for use in glass-reinforced high temperature polyamides. A more recent disclosure shows that the glycidyl methacrylate-bromostyrene copolymer gives greatly improved blistering performance in surface mounting electronic technology applications [33].

Another approach to compatibilization of the brominated polystyrenes with a polyamide is to add a functional polymer as a compatibilizing agent. This is shown in a recent patent application by DSM where a styrene-maleic anhydride copolymer (Dylark® 232 or 250) is used at 2–8 % in a blend of polyamide 4,6 (DSM's Stanyl®) with a brominated polystyrene (Great Lakes PDBS 80) plus Sb₂O₃, giving better flame retardancy and in some cases better toughness [34]. Addition of small amount of polyamide 6 or low molecular weight polyamide 4,6 helps in compatibilization of Stanyl with PDBS 80 [35]. A small amount of polyvinylpyrrolidone (~1.0 wt. %) also has a beneficial effect of suppressing dripping, so the use of PTFE can be avoided [36]. Albemarle found that a small amount of polyethylene or polypropylene helps with compatibilization of brominated polystyrene in polyamide 6 [37].

Some discoloration that occurs at the high temperature of solder reflow with polyamide 4,6 can be avoided by eliminating the antimony oxide and using as synergist zinc borate or zinc stannate plus a phosphite stabilizer [38]. Hydrazine sulfate, hydrazine borate or 1,1-diphenylhydrazine help to prevent discoloration in glass-filled polyamide 6.6 according to Japanese research [39].

The bromine-containing polystyrenes lend themselves to the production of free-flowing pellets containing antimony oxide. Several of these are available from Chemtura or Albe-marle.

5.2.2.5 *Brominated Epoxy Oligomers as Additives*

For high temperature processing of polyamides, there are some advantages to use of brominated epoxy oligomers which are derived from tetrabromobisphenol A and epichlorohydrin [40]. These are available from ICL-IP as the F-2400 series. They are melt-blendable and impart good processing and mechanical properties, particularly impact. They also have high UV stability and are non-blooming. A typical formulation in 30 % glass-filled polyamide 6 uses 19 % F-2400, 3.7 % antimony oxide, and gives V-0 rating at 1.6 mm thickness. Tensile strength is 118 Mpa, notched Izod is 103 J/m and elongation at break is 3.9 %. Being high molecular weight materials, their toxicology is favorable.

Recently, ICL-IP introduced a new grade of brominated epoxy, F-3100, end-capped with tribromophenol [41, 42]. Low adhesion to the surface of processing equipment is the main advantage of this new grade [43]. Because of good melt flow properties F-3100 offers compounds and molders energy savings during the processing. It is also beneficial in scrap recycling. F-3100 can be used alone or in combination with brominated polystyrene, where it improves melt flow and gloss properties in glass reinforced polyamides.

A comparison of this family of oligomers to other bromine and non-bromine additives used in polyamide 66 is shown in Table 5.2.

These polymeric brominated additives appear favorable in regard to strength, modulus and impact relative to the non-polymeric brominated additive.

5.2.2.6 *Poly(pentabromobenzyl Acrylate as Additive; Comparison with Other Bromoaromatic Additives*

This polymeric additive, available from ICL-IP as FR-1025, serves not only as a flame retardant but also as a processing aid [45]. Although higher priced than some other polybrominated aromatics, it has features of non-blooming, high temperature and weathering resistance, good electrical properties and good compatibility with fiber reinforcement.

A comparison by Ameribrom (ICL-IP) of this product with other bromoaromatic additives discussed above as flame retardants for glass-reinforced polyamide 6 is shown in Table 5.3. The choice amongst these additives will depend on the property to be emphasized, and cost.

5.3 **Melamine Cyanurate**

This solid additive permits “halogen free” marketing. A good review, specific to this retardant, was published in 1994 [47]. It appears to work by producing enhanced dripping (with non-burning drips) and also by dissociating endothermically to produce non-combustible vapor [48–50]. Especially in polyamide 66, it also somewhat enhances the thermal degradation residue. Ratings of UL 94 V-0 can be obtained at 5–10 wt. % in unreinforced polyamide

Table 5.2 Properties of Flame Retardant 30 % Glass-Reinforced Polyamide 66 with Various Flame Retardants at UL 94 V-0 Rating (Tradenames from ICL-IP) [44]

Fire retardant type	Decabromo-diphenylethane	Phosphinate salt	Brominated polystyrene (FR-803P)	End-capped medium M_w brominated epoxy (F-3100)
Composition %				
Polyamide 66	51.4	52	45.6	42.3
Glass fiber	30	30	30	30
FR system*	18.6	18	24.4	27.7
Properties:				
UL 94 class at 0.8 mm	V-0	V-0	V-0	V-0
Spiral flow (300 °C), in.	38.4	35	36.2	41.2
Tensile:				
Yield strength, MPa	140	128	152	173
Elong. at break, %	2.4	2.8	2.6	2.1
Modulus, MPa	9 500	7 700	11 500	11 400
Heat distortion temperature, °C	197	201	200	200
Notched Izod, J/m	78	95	96	99
CTI, V	300	600	400	350

* includes synergist and antidripping agent

66, at 8–15 wt. % in unfilled polyamide 6, and at 13–16 wt. % in some mineral filled polyamide formulations. However, it is difficult to reach V-0 in glass filled polyamide; V-2 can be reached at about 10–13 %. Polyamides 11 and 12 need a higher dosage, around 15 wt. %. About 20 wt. % melamine cyanurate is needed in order to pass the glow wire test at 775 °C [51]. The reason for melamine cyanurate's somewhat better activity in polyamide 66 than in polyamide 6 has been explained: polyamide 66 tends to pyrolyze to form cyclopentanone, which condenses with the melamine and/or cyanuric acid formed by dissociation of melamine cyanurate causing crosslinking and residue formation. On the other hand, the pyrolysis of polyamide 6 yields mostly caprolactam, alkyl cyanides and ammonia which do not interact much with the melamine cyanurate pyrolysis products [52]. In polyamide 6 melamine cyanurate decreases the yield of caprolactam, but increases yield of oligomeric fragments, which are less flammable, but help to enhance melt-flow [53].

The reason for the interference by glass reinforcement in the action of melamine cyanurate has not been completely elucidated. The glass fibers obviously retard melt flow and act as a "wick". Moreover, they may provide more heat flow into the interior of the polymer. There have been reports that very short glass fibers can be tolerated. It was also shown that melamine cyanurate provide V-0 rating in mineral filled polyamide 6 [54] or polyamide 66 [55].

In filled polyamides, melamine cyanurate may be found useful in combination with magnesium hydroxide [56]. A melamine cyanurate variant, Ciba's MC-XL, with improved process-

Table 5.3 Properties of Flame Retardant 30 % Glass-Reinforced Polyamide 6 with Various Brominated Flame Retardants at UL 94 V-0 Rating (Tradenames from ICL-IP) [46]

Fire retardant type →	Poly(penta-bromobenzyl acrylate) (FR-1025)	High M _W brominated epoxy polymer (F-2400)	End-capped medium M _W brominated epoxy (F-3100)	Brominated polystyrene (FR-803P)
Composition %				
Polyamide 6	51.3	46.9	46.7	45.7
Glass fiber	30	30	30	30
Flame retardant	12.9	17.3	17	19.4
Antimony trioxide	5.7	5.7	6.2	5.7
PTFE antidrip	0.1	0.1	0.1	0.1
Bromine content %	9	9.2	9	12.8
Properties				
UL 94 class at 0.8 mm	V-0	V-0	V-0	V-0
Spiral flow (290 °C), in.	41	28	41	33
Tensile				
Max. strength, MPa	159	170	155	149
Elong. at break, %	2.3	2.4	2.4	2.5
Modulus, MPa	11 000	11 700	8 900	10 400
Heat distortion temperature, °C	197	201	200	200
Notched Izod, J/m 23 °C	129	82	100	68

ability in polyamides, and giving less toxic and visible smoke, has recently been reported [49].

Chinese researchers [57, 58] have shown that melamine cyanurate can be formed in situ from melamine and cyanuric acid in polyamide 6 in reactive extrusion processing. This approach gave poorer tensile strength but improved impact and flame properties compared to addition of pre-formed melamine cyanurate, and it could lower the cost.

Addition of melamine cyanurate even in small amounts (5 wt.%) deteriorates melt-flow properties of polyamide. A DuPont patent [59] shows use of long chain amides or esters (N-stearylseramide, ethylenebis-stearylamide), behenic acid monoglyceride or stearyl stearate) to significantly improve melt flow of polyamide 66.

Combinations of melamine cyanurate with a tetraaryl arylene diphosphate are shown to be effective flame retardants in a variety of polyamides, but to avoid stiffness (presumably caused by the melamine cyanurate), a polyol such as pentaerythritol or dipentaerythritol must be added according to a Degussa patent [60].

Because of the lower concentration of amide groups, melamine cyanurate is not as effective in polyamide 11 and polyamide 12 as it is in polyamide 6 and 6,6. To improve efficiency, an

Atofina patent [61] suggests using combinations of melamine cyanurate, antimony trioxide and pentaerythritol, preferably in the form of a concentrate.

5.3.1 Other Melamine Additives

DuPont has developed formulations for polyamide 66 making use of melamine pyrophosphate [62]. A favorable combination of flame retardant properties and mechanical properties is shown at 28–29 % melamine pyrophosphate plus 20 % chopped glass. The product is light in color and retains good elongation and tensile strength, comparable to halogen-retarded polyamides. Extrusion temperature must not exceed 325 °C which is the decomposition temperature of melamine pyrophosphate. One way to avoid damage to the polyamide is to make a minor molecular modification [63] or coating of the additive [64] or add a processing aid to lower the processing temperature into a safe range. It is even possible to lower the processing temperature sufficiently, to below about 250 °C, in a copolymer of polyamide 6 and 66 so that melamine itself can be used as flame retardant [65]. In order to increase the efficiency of melamine pyrophosphate, DuPont researchers suggested synergizing it with phosphotungstic or silicotungstic acid [66, 67].

In these melamine pyrophosphate formulations, it was found that replacing some of the melamine pyrophosphate by zinc borate greatly increased the CTI [68]. A broad review of combinations of zinc borate with phosphorus flame retardants and other non-halogen systems has been presented by Luzenac researchers [69].

Melamine polyphosphate (DSM's Melapur® 200; now Ciba's) also performs reasonably well in polyamide 66, and may have some advantages [70]. In glass-filled polyamide 66, it was shown by Ciba researchers to be superior to red phosphorus and to a bromine-antimony system in regard to smoke density and carbon monoxide yield [71]. Both melamine polyphosphate or pyrophosphate perform less well in polyamide 6 because of the depolymerization mode of decomposition of this polyamide. In polyamide 66, they cause char formation, as well as having a blowing agent effect. They are most effective in glass filled systems (in complete contrast to melamine cyanurate) because the glass fiber supports the char. The polyphosphate appears to have somewhat higher thermal stability than the pyrophosphate, and undergoes only 0.7 % weight loss at 325 °C. In DSM's study of melamine polyphosphate in polyamide 66, a large advantage was found in opacity and corrosivity of the smoke with the phosphorus additive compared to a halogenated additive [70]. Even more thermally stable than melamine polyphosphate is melam polyphosphate which is mentioned in some Mitsubishi patents [72], however real commercial success of this flame retardant is not clear.

In non-halogen flame retarding of polyamide 4,6 (DSM's Stanyl®), melamine polyphosphate (Melapur® 200) can be used despite the high processing temperature (with Stanyl itself, above 340 °C) by including some polyamide oligomer which reduces the processing temperature [73]. A V-0 rating is reached while retaining acceptable impact and tensile strength. Melamine polyphosphate can also be used in a copolymer of polyamide 66 and isophthalic acid aromatic polyamide in spite of the high processing temperature [74]. In fact, melamine polyphosphate is more effective in this co-polymer than in plain polyamide 66. Recently, Clariant researchers patented the stabilization of melamine polyphosphate with 2–5 wt. % zinc oxide or zinc borate

[75]. A combination of melamine polyphosphate and molybdenum trioxide is beneficial because of high arcing resistance [76].

5.4 Inorganic Hydrates

5.4.1 Magnesium Hydroxide

Polyamide 6 can be successfully flame retarded to a V-0 standard at 1.6 mm thickness, using about 60 % loading. This product has a good color and high CTI, but is difficult to process and is rather stiff [77]. In general $\text{Mg}(\text{OH})_2$ is not recommended for use in glass-filled polyamides, however formulations of polyamide 6 with low loading of glass fibers (8–15 %) are known [78]. Special grades of magnesium hydroxide with uniform crystals and low surface area are more preferable for polyamides because of high thermal stability up to 340 °C [79]. A special grade of $\text{Mg}(\text{OH})_2$ with hexagonal shaped crystals and a particular specific aspect ratio was recently patented by Kyowa [80].

It has been shown [81] that the mode of flame retardant action of $\text{Mg}(\text{OH})_2$ in polyamides is different from the action in polyolefins where $\text{Mg}(\text{OH})_2$ is used more often. Magnesium hydroxide at 60 % loading increases the oxygen index of polyamide 6 by 205 %, polyamide 66 by 120 %, whereas polypropylene only by 50 %. It is believed that $\text{Mg}(\text{OH})_2$ promotes charring of polyamides by reacting with products of thermal decomposition (probably acids).

Magnesium hydroxide activated with small amounts of catalytic metals, for instance $\text{Mg}_{0.96}\text{Zn}_{0.02}\text{Ni}_{0.02}(\text{OH})_2$ is effective in giving a V-0 rating at as low as 33 % [82]. Combinations of magnesium hydroxide with red phosphorus (see below) have been found to be useful for electrical parts. Lanxess [83] discloses flow benefits of including 1–10 % of illite (a layered micaceous clay) in glass-reinforced polyamide 6 flame retarded with magnesium hydroxide. It was also found that $\text{Mg}(\text{OH})_2$ is synergistic with phenolformaldehyde novolac resin, *e.g.*, 53 wt. % $\text{Mg}(\text{OH})_2$ + 4 wt. % novolac provide a V-0 rating in polyamide 6 and 66 [84]. 15 wt. % $\text{Mg}(\text{OH})_2$ with 10 wt. % melamine cyanurate is a beneficial combination for passing the glow wire test for polyamide 6 or polyamide 66 with low glass-fiber loading (10 %) [85].

A comparison of the effects on comparative tracking index of various flame retardants for 10–20 % glass-filled polyamide 6 was presented by Albemarle [26]. This showed a large CTI advantage for magnesium hydroxide (Albemarle's Magnifin®) compared to no flame retardant, and compared to two brominated additives with antimony oxide.

5.4.2 Alumina Monohydrate

Alumina trihydrate (ATH) loses its water at too low a temperature to be used in typical polyamides but the monohydrate (boehmite) at 2–200 nm crystallite size is dispersible in polyamides and can give a flame retardant effect (not specified) but mainly increases the modulus [86, 87].

5.5 Phosphorus Additives

5.5.1 Red Phosphorus

Red phosphorus, the thermodynamically stable high-polymer form of phosphorus is, weight for weight, the most effective phosphorus flame retardant [88]. Its use has been deterred by problems of color, handling safety and stability. However, much progress has been made in stabilizing and coating or encapsulating red phosphorus and the handling problems with the powder have been overcome by the commercial availability of masterbatches in a variety of polymers and polymer precursors. Usage is now well established in glass-reinforced polyamide 6,6, using stabilized coated red phosphorus. Red phosphorus is especially favorable for polyamide 6,6 because of the high processing temperature of this polymer (often above 300 °C) where many phosphorus-based flame retardants cannot survive [89]. It is quite well established in Europe and the Far East, and sales in the US are now underway.

Much of the technology of improving red phosphorus has to do with avoiding a slow reaction under the combined action of oxygen and water forming small amounts of toxic and malodorous phosphine gas (PH_3) and corrosive phosphorus acids. In general, phosphine generation during polymer processing can be minimized by use of a stabilized and coated version of red phosphorus such as available in the Clariant's Exolit® RP series of powders, dispersions and concentrates, by moderating the temperature and by adequate drying of the polymer. Where very strict electrical requirements, such as very high tracking resistance, must be met, Clariant's Exolit RP 69X may be found suitable. Red phosphorus can be enhanced as a means for achieving a glow wire ignition temperature of greater than 750 °C in polyamide by addition of a divalent or trivalent metal phosphate or pyrophosphate, such as calcium pyrophosphate [90] or melamine polyphosphate with a nanoclay [91].

Zinc borate, zinc oxide or iron oxide help retard the corrosive effect of phosphine, and may also enhance the flame retardant action [68, 92]. A recent patent application by Bayer [93] shows use of specific combination of 0.7 wt. % ZnO , 0.7 wt. % talc and 0.01 wt. % cerium oxide (CeO_2) as a stabilizing package with 6 wt. % red phosphorus. A recent Chinese study [94] shows a process of deposition of melamine cyanurate on the surface of red phosphorus, which is said to provide better compatibility with polyamide and enhances flame retardant efficiency.

The use of commercially available masterbatches avoids the hazards of handling the powdered red phosphorus; it also avoids or minimizes any phosphine evolution or other decomposition during mixing by a polymer compounder.

The largest use of red phosphorus as a flame retardant in Europe (particularly in Germany and Italy) appears to be in polyamide 66 by BASF. Some types of end-products in which it is used are electrical connectors and switchboxes, where often the red color is acceptable. The low level of additive required, in the 7 % range, permits better tensile and impact strength than the halogen systems which typically require about 18–25 % additive. Another advantage claimed for the red phosphorus is in electrical tracking resistance. Data on a 25 % glass filled PA 66 flame retarded to a V-0 rating with 12 % of Italmatch's Masteret® 20450 red phosphorus masterbatch shows a CTI of > 600 V, with excellent tensile strength and impact. Recent patents to BASF show use of small amount of polyolefin polymer (4–6 wt. %) to

improve compatibility [95]. The use of 0.5–2.0 wt. % black pigment with a dispersing agent helps to mask the red color [96].

In spite of its apparent chemical simplicity, the mode of flame retardant action of red phosphorus in polyamides is complex and has been a subject of several academic studies. It seems that recent publications have come to the consensus that red phosphorus depolymerizes to white phosphorus, which partially evaporates and acts as a gas phase inhibitor and partially reacts with polyamide and enhances charring [97–99].

5.5.2 Aluminum Dialkylphosphinates

Various salts of dialkylphosphinic acids, including aluminum, were first noted as flame retardants by Sandler (Pennwalt) but not commercially pursued at the time. They were commercially developed by Hoechst, later Clariant and Ticona, and appear quite active in a range of thermoplastics and thermosets, including polyamides [100]. A V-0 rating can be obtained in unreinforced polyamide 6 with 15 % loading of aluminum methylethylphosphinate and at 30 % loading in glass reinforced polyamide 6. Aluminum diethylphosphinate, Clariant's Exolit® OP 1230, is now the leading member of the phosphinate flame retardant group, and probably has lower manufacturing cost. Two other members of this family, Exolit OP 1311 (a synergistic blend) and 1312 (as 1311 but some additional zinc borate as thermal stabilizer) have been commercialized and have been reviewed by a Clariant researcher [101] who emphasizes that the low levels of addition, 15–18 % to reach UL 94 V-0 at 0.8 mm, permits good retention of mechanical properties. The Clariant researchers [102, 103] present a comparison of the loadings necessary to reach UL 94 V-0 and the more difficult UL 94 5V A at various thicknesses in 25–30 % glass — at $\frac{1}{32}$ ", polyamide 6 requires 20 % Exolit OP 1311, polyamide 66 requires 18 % Exolit OP 1312 and high temperature polyamide PPA requires 12 % of Exolit OP 1230. The same study presents data showing good glow wire ignition results, retention of mechanical properties, light stability, combustion toxicity and recyclability. A further Clariant presentation [104, 105] compared the required dosage of various additives to reach V-0 in a 30 % glass polyamide 66: red phosphorus, 7 %; Exolit OP 1312, 16 %; Dechlorane Plus, 20 %; melamine cyanurate, 20 % but only reaches V-2; brominated polystyrene and Sb_2O_3 , 26 %. With Exolit OP 1312, the polyamide is stable to lead-free soldering, has good flowability, and good mechanical, electrical and recyclability properties. Comparative tracking index (IEC 112) is 600 V for the Exolit OP 1312 but only 400 V for the brominated polystyrene. One additional advantage of phosphinates is the low specific gravity of molded polyamide parts, which could be 15–20 % lower than parts molded with brominated flame retardant [106]. Good results in the glow wire test were achieved with polyamides containing phosphinates [107]. The Glow Wire Flammability Index was passed at 960 °C and the Glow Wire Ignition Temperature was achieved at a level of 775 °C.

Nitrogen synergists are highly effective with the phosphinate salts; a V-0 rating can be obtained in polyamide 6 with 8 % melamine cyanurate and 8 % aluminum methylethylphosphinate [108]. Combinations of the aluminum phosphinates with ATH, aluminum phosphates or aluminum phosphonates are also highly effective in polyamides [109]. Clariant has shown that melamine polyphosphate (Ciba's Melapur® 200) is also an excellent synergist with

aluminum diethylphosphinate in glass-reinforced polyamide 66 [110]. To avoid some decomposition in this type of formulation, the addition of a stabilizing amount of zinc hydroxide carbonate [111], zinc oxide or zinc borate [112] (presumed acid acceptors) was shown in a Clariant patent to be advantageous.

Glass-reinforced blends of polyamide 6 and 66 with poly(phenylene ethers) can be flame retarded to V-0 with as little as 8 parts of aluminum diethylphosphinate with good retention of impact strength [113–115] and show highly effective combinations of the phosphinate salts with a wide range of heterocyclic nitrogen compounds plus any of a wide range of aromatic polymers, and glass fibers, optionally with a nanoclay.

A study in Hungary [116] found that in polyamide 6, the phosphinate salt flame retardants could be synergized as well by unmodified montmorillonite as by the more expensive modified quaternary ammonium modified clay. German researches studied the mechanism of flame retardant action of aluminum diethylphosphinate in polyamide 6,6 [117]. They found that pure phosphinate mostly provides a gas phase mode of action, however when melamine polyphosphate is added, the mode of action shifts to the condensed phase and insulating char barrier action becomes even more pronounced with addition of zinc borate.

Aluminum dimethylphosphinate or calcium ethylmethylphosphinate was shown in an EMS patent application [118] to be effective in flame retarding fiber reinforced polyamide 66 blended with partially aromatic polyamides, while allowing high heat deflection temperatures. A Clariant patent application [119] and Solvay patent application [120] also shows good flame retardant results (V-0) with dialkylphosphinate salts in aromatic or semiaromatic polyamides.

5.5.3 Hypophosphite Salts

Aluminum hypophosphite (Italmatch's Phoslite® A) [121] is an efficient flame retardant in polyamides. A formulation of 77.5 % polyamide 6 (Latamid 6B-30 % glass), 7 % aluminum hypophosphite, 15 % melamine cyanurate and 0.5 % sorbitan dioleate gave a V-0 rating at 3.2 mm and V-1 at 1.6 mm.

5.6 Drip Retarding Additives

Finely divided (actually microfibrillated) polytetrafluoroethylene has been frequently used to retard drip in flame retardant polyamides, and by doing so, it is sometimes possible to go from a UL 94 V-2 rating to a V-0 rating. Effective PTFE grades include DuPont Teflon® 60 or Hoechst's Hostaflon® 9202 or 1665.

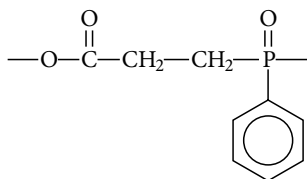
"Nanoclays" (exfoliated montmorillonites) can also serve as anti-drip additives at levels of 1–3 %, also providing increased char formation and char strength, as well as a flame retardant effect (especially in combination with other flame retardants such as decabromodiphenyl ether and antimony oxide) [122].

5.7 Treated Glass Fiber Reinforcement

French investigators [123, 124] have found that suitable sizing treatment of the glass fiber reinforcement in polyamide 6 enables it to be flame retarded with melamine cyanurate or melamine (pyro- or poly-)phosphates. Suitable sizing agent components are pentaerythritols, ammonium or guanidine phosphates or pyrophosphates or potassium nitrate (nitrates apparently promote char [125]).

5.8 Textile Fiber Applications

Despite much effort, no successful coreactant or additive flame retardant has been found for polyamide 6 or 66 textile fiber. A difficulty with additives is that any particulate solid or even melt-blended polymer forming a separate phase will greatly reduce the strength of the melt-spun fibers. A long-term effort was made at Monsanto to introduce, in place of part of the adipic acid, a phosphine oxide-containing dicarboxylic acid $\text{RP(O)(CH}_2\text{CH}_2\text{COOH)}_2$, R = alkyl or aryl. Although properties of the thus-modified polyamide 66 fiber were encouraging, economics were unfavorable, and despite much effort at Monsanto and by hopeful suppliers of the acid, no commercialization resulted [126]. More recently, Solutia developed a reactive intermediate Phosgard® PF-100 that can be used to introduce a phosphinate unit (see structure below) into the polyamide chain to obtain flame retardant fibers or molding resin [127]. This technology has been offered for commercialization; current status is uncertain. It appears to be in development by at least one Chinese company.



Textile finishes for flame retarding polyamide fabrics has been available for many years. One of the well-established ones is a thiourea-formaldehyde resin, thermally cured with acid catalyst. It is sold as Bayer's Flamegard® 906 or in methylated form as Flamegard® CNX. The mode of action is probably the lowering of the melting point and melt-flow enhancement.

Other finishes or backcoatings which are workable on polyamide fabrics, as well as on most other fabrics, are based on decabromodiphenyl oxide or hexabromocyclododecane, antimony oxide and a polymeric binder.

Polyamide carpets, which dominate the synthetic fiber carpets in the US, tend to pass the carpet flammability methenamine pill test with no need for a flame retardant. Their melting behavior is probably responsible for this. The elastomeric backing is commonly filled with calcium carbonate, which is more of an inert diluent than a true flame retardant. In the instances where stringent flammability standards are imposed, as might be the case with contract carpeting for public buildings, alumina trihydrate may be used in the latex backing material as an endothermic flame retardant. A few constructions, such as shags, can fail even

the rather lenient methenamine pill flame retardancy test and in these cases, Dechlorane Plus® or a suitably stable polybrominated aromatic additive (as discussed earlier) may be added to the fiber melt before spinning [128]. Polyvinyl chloride or chloroparaffin emulsion can also be applied to the face side of the primary backing.

For more demanding polyamide carpet requirements, such as on aircraft, flame retardancy of the pile, the backing and the latex binder is often needed. A Japanese product [129] uses melamine cyanurate of less than 5 micron size to flame-retard the pile yarn and the backing is flame-retarded by a latex containing, for example, expandable graphite and ammonium polyphosphate.

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6 Flame Retardants for Thermoplastic Polyesters in Commercial Use or Development

6.1 Introduction

The principal polyesters covered in this chapter are polyethylene terephthalate (PET), polybutylene terephthalate (PBT), poly(cyclohexanedimethanol terephthalate) and the relatively new poly(1,3-propanediyl) terephthalate or poly(trimethylene) terephthalate (PTT). There are also hybrid products with two different glycol or acid components. Another family of polyesters is made from both aromatic diols plus aromatic dicarboxylic acids; these are the polyarylates, which are inherently flame resistant. These are all molding resins; in addition, PET has major film and textile fiber applications, and PBT is also entering that use area. The major use of PBT is in injection molded products, where it has the advantage of being fast-crystallizing, allowing for rapid cycling in molding. In regard to PET, we will discuss both the molding resin and the textile flame retardancy technology; however, polyester fiber blends will be discussed in the chapter on textile flame retardancy.

Where information is stated without a reference, its source may be assumed to be product literature of the manufacturer.

Confidentiality maintained for many formulations prevents us from being certain of the actual commercial use or development of some patented compositions, but we have included such patents or patent applications where convincing examples were given.

6.2 Polyethylene Terephthalate

6.2.1 Textile Fiber Flame Retardance by Melt-Spinning Additives

PET used in carpets requires no flame retardant to pass the Federal “pill test,” because of its melting tendency. Some carpets for high risk occupancies must pass a more stringent radiant panel test; in some cases, alumina trihydrate (ATH) is used in the backing as an endothermic flame retardant. PET in ordinary apparel constructions easily passes the Federal apparel standard requiring a lenient 45° angle rate-of-burn test. Moreover, PET without a flame retardant can pass the Federal children's sleepwear standard which uses a bottom-ignition vertical test with char length limitation; this is because in the present version of this test, burning drips are allowed. An earlier version did not allow burning drips, and consequently the flame retardant tris(dibromopropyl) phosphate (later found to be mutagenic) was used for a time.

There is some market for inherently flame retardant PET fiber and fabric, for upholstery and draperies, for instance in hotels, motels and institutions, and in apparel for high risk situations such as nursing homes.

One of the earliest products of this type was Toyobo's HEIM, a PET fiber flame retarded by a phosphorus additive, oligomeric sulfonylbisphenol phenylphosphonate added at about 7–9 %. This oligomer was developed from earlier members of the phenylphosphonate oligomer family by a systematic search for the best combination of activity, stability, miscibility and cost [1]. It has a well-matched solubility parameter with PET, according to a Chinese study [2] and is thus miscible over a wide range. Levels below 15 % are of most interest for flame retarding of PET. This system has also good light-fastness and is more easily dyed with disperse dyestuffs than conventional polyester fibers [3].

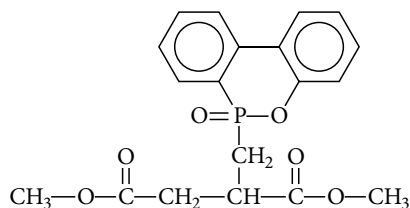
The sulfonyl group probably contributes some flame retardancy itself, and it causes the bisphenol to be more acidic than an ordinary bisphenol, so that the phosphonate ester linkage is rather anhydride-like, which probably facilitates interaction with the PET during pyrolysis.

This oligomer is also believed to be produced and used in China for use in PET textiles. It also has been shown to be of some value as a flame retardant component for PBT. However, in PBT, to pass the UL 94 V-0 standard (much more stringent than textile tests), it needs further enhancement by char-forming ingredients such as PPO and volatile ingredients such as triphenyl phosphate [4].

After some years of commercial usage of this oligomer by Toyobo, problems of hydrolysis and dye shade changes appear to have been the motivation for Toyobo to change to a PET modified by a phosphinate structure in a side chain, discussed below

6.2.2 Dihydrooxaphosphaphenanthrene Reactant in Polyethylene Terephthalate

The subsequent development by Toyobo in Japan was the reaction product of dihydrooxaphosphaphenanthrene oxide (DOPO) with itaconic diester to make a phosphinate diester which can be reacted into the PET molecule. The structure is as follows [5, 6]:



Some process details (efforts at simplifications) have been published [7]. This product, now designated as HEIM, displaced Toyobo's earlier phenylphosphonate oligomer as the better means for introducing inherent flame retardance without sacrificing desirable mechanical, dyeing and aging properties. Several features can be discerned in this molecule: first, the phosphorus is in a thermally stable and sterically hindered phosphinate structure which is relatively resistant to hydrolysis. Secondly, if hydrolysis does occur, the phosphorus is not lost nor is the PET backbone disturbed. The hydrolysis resistance also gives this side-chain phosphinate an advantage over the KoSa product discussed below, which has the methylphosphinate built into the backbone of the polyester. After being subjected to hydrolysis by aqueous acetic acid at pH 4 for 1–6 hours at 130 °C, the side-chain phosphinate-modified

PET showed only about half the hydrolytic cleavage that the main-chain phosphinate-modified PET showed, and thus fiber tenacity was better maintained for the side-chain modified polymer [8, 9].

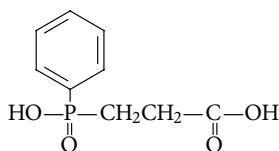
Because of the hydrolytic resistance, HEIM fabric has no change in texture and no shrinkage after a boiling treatment of 5 minutes or a sterilization steam treatment with 120 °C steam for 3 minutes. Loss in strength under hydrolytic conditions is also minimal since the phosphorus ester bonds are not in the main chain of the polymer. However, addition of the bulky phosphorus group decreases crystallinity of PET and decreases melting point [10].

The flame retardancy of HEIM is mostly achieved by the melt drip effect promoted by the degradative effect of the polyphosphoric acid produced in burning.

On the disadvantageous side, DOPO involves many synthesis steps from a specialty phenol. The cost of DOPO may be lowered by development of other uses which have been found for it, for instance it is useful as an antioxidant stabilizer and as a reactive flame retardant for epoxy resins in printed wiring boards. Alternative technology was developed at Nippon Ester, where PET was first copolymerized with the unsaturated acid (such as itaconic) and afterwards reacted with DOPO [11], however it is not clear if this route was commercialized.

HEIM is available as both filament yarn and staple fiber. A spunbonded non-woven fabric is available made from HEIM. Main uses for HEIM are in interiors, particularly bedding, walls and floor finishings, and industrial materials, such as in the aviation and automotive fields. Films are also available and used for packaging and other industrial applications. New applications of HEIM are in flame retardant paints, using an organic-soluble version, and hot melt adhesives, using an organic-insoluble partly crystalline version.

Apart from Toyobo, this type of reactive monomer is also available in Europe from Schill & Seilacher under the trade name Ukanol® FP50 (see structure below, solution in ethylene glycol) and probably also from Kolon Industries [12] in Korea. A recent Russian study on pilot plant scale production [13] showed easier reaction of Ukanol to form PET copolymer compared to Avora® CS (see below). A similar comparative reaction study is available for HEIM and 3-(phenylphosphinyl)propanoic acid (see below), which also favors HEIM [14].



Self-extinguishing PET films using the above-described DOPO-itaconic ester coreactant are also described in a patent to DuPont Teijin Films [15].

A related modified PET for textile fibers, using the $(\text{C}_6\text{H}_5\text{O})(\text{C}_6\text{H}_5)\text{P}(=\text{O})\text{H}$ adduct of itaconic ester instead of the DOPO adduct has been patented in many countries by Sanyo Chemical Industries [16]. Its commercial status is not evident.

6.2.3 Phosphinate Structure in PET Backbone

Another approach was developed at Hoechst in Germany, and continues to be one of the leading means for building a flame retardant structure into PET. The synthesis of the intermediate is from methylphosphinic acid, which is reacted with acrylic acid to produce a diacid of the structure $\text{HOP(=O)(CH}_3\text{)CH}_2\text{CH}_2\text{C(=O)OH}$. This diacid is converted to a cyclic anhydride and then to a glycol ester, at which stage it can be reacted into the PET esterification [17, 18]. The resultant fiber can be made into disperse-dyeable staple fibers, 1.3–3 denier suitable for making fabrics to pass FF3-71, NFPA 701 and CS-91 method 5903. The fiber is KoSa's (now Koch Industries') Avora® CS. It is preferably used in 100 % polyester fabric, not in blends. The principle applications are in home or hotel furnishings (bedspreads, draperies), hospital cubicle curtains, and special apparel for fire-risk situations [19].

An analogous product was made from 3-(hydroxyphenylphosphinyl) propanoic acid $\text{HOP(=O)(C}_6\text{H}_5\text{)CH}_2\text{CH}_2\text{C(=O)OH}$ at Monsanto [20, 21] and is currently in use in Asia [22]. Introduction of this unit into the PET backbone does provide flame retardancy but reduces the hydrolytic and thermal stability of the PET more than does introduction of the DOPO-derived diester unit discussed in the preceding section [23]. The joint incorporation of this diacid or its P-methyl analog along with the DOPO-based diester discussed above has been described as a means for making flame retardant PET fibers in a Schill and Seilacher patent application [24].

6.2.4 Mode of Action of Phosphorus Flame Retardants in Polyethylene Terephthalate Fabrics and Materials which Interfere with this Action

As mentioned in the discussion of HEIM, the mode of action of these phosphorus flame retardants seems to be mainly melt-flow enhancement. If the flow is impeded by solids, which can provide the equivalent of a "wick", the flame retardancy is badly compromised. Thus, blends with cotton cannot be made, and all materials which might give an infusible solid such as silicone spinning lubricants and sewing lubricants, print pigments, and sizes must be avoided [25, 26].

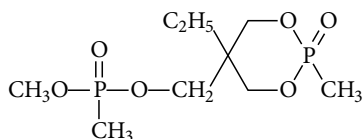
6.2.5 Bromine-Containing FR in PET Fibers

A PET variant which involved use of bis(2-hydroxyethyl) ether of tetrabromobisphenol A was introduced in the 1970s on a development basis by DuPont (Dacron 900 F) [3] but seems not to have found demand commensurate with the cost or price.

Recently, Kaneka applied for a patent on use of high molecular weight (30 000–40 000) brominated epoxy oligomers in PET fibers [27]. Because of the high molecular weight the additive doesn't compromise physical properties at 10 wt. % loading and provides immediate extinguishment of the flame.

6.2.6 Flame Retarding Polyethylene Terephthalate Fabric by a Thermosol Finishing Process

A highly successful approach has been to introduce a flame retardant amount of phosphorus by applying a thermally stable phosphorus ester which is then “thermosoled” into the fabric by heating to a temperature at which incipient softening of the polymer occurs. This is similar to the process of disperse dyeing, which involves a thermosol step to get the dye to penetrate and become locked in on cooling. The principle phosphorus compound found suitable for this process is Antiblaze® NT or (former Antiblaze® 19, now Rhodia’s Amgard CU or Special Materials SM688), a diphosphonate product made from trimethylolpropane phosphite and dimethyl methylphosphonate [28, 29]. It has the following structure:



This method for flame retarding polyester fabric is highly successful and many commercial formulations of Antiblaze NT are available from a number of textile chemical formulators with various wetting and perhaps penetrating agents. The inclusion of urea in the pad bath appears to enhance the penetration, and surfactants may be helpful for assuring even wetting and penetration. It is also advantageous to buffer the solution to pH 6.0–6.5 using disodium phosphate.

To produce flame retardant polyester fabrics passing DOC FF3-71 and NFPA 701, about 1.0–1.5 % of the phosphonate (about 0.2–0.3 % P) is generally needed. Usually this can be accomplished by about applying 8–15 % wet pick up of the diluted phosphonate solution. On the basis of 100 % active ingredient, this is about 3–6 % on the weight of the fabric. After drying at about 107–135 °C for 1–2 minutes, the fabric should be subjected to thermosol conditions, about 182–204 °C with a dwell time of 30–45 seconds, then cooled and rinsed free of unfixed chemicals. Typical fixations are in the range of 40–50 % on the weight of the fabric. A recent patent application to Wellman [30] discloses a formulation containing 0.15 wt. % P, 4.0–7.0 wt. % Br and 1.5–2.0 wt. % Sb to pass the California CAL 604 test for bedding filler.

It is possible that other phosphorus compounds can be used in the thermosol process; an example is treatment with naphthyl diphenyl phosphate, as claimed by Daiichi Kogyu Seiyaku [31] or with biphenyl diphenyl phosphate [32]. Similar applications of naphthyl or biphenyl phosphates are disclosed by Daihachi [33]. A pressure dyeing method using various aromatic diphosphates is claimed by Nippon Kayaku [34].

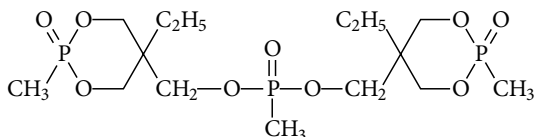
6.2.7 Flame Retarding Polyethylene Terephthalate Molding Resin by an Aromatic Diphosphate

PET moldings with good dimensional and thermal stability are disclosed by Toray Industries [35] using tetrakis(2,6-xylyl) m-phenylene diphosphate (Daihachi PX-200), melamine cyanurate, glass fiber and mica.

A complex flame retarded formulation of 35.1 % PET, 13 % PX-200 (tetrakis(2,6-dimethylphenyl) resorcinol diphosphate), 5 % phenol formaldehyde resin, 10 % melamine pyrophosphate, 33 % glass fiber and small amounts of various stabilizers is shown in a Du Pont patent application; good mechanical properties in molded articles are claimed [36].

6.2.8 Flame Retarding Polyethylene Terephthalate by other Phosphorus-Containing Additives

A low-volatility triphosphonate, Antiblaze® 1045 (Albright & Wilson, later Rhodia's Amgard 1045) can be used as an additive in molded PET and probably in melt-spun PET. This product is related to the Antiblaze® NT (CU) discussed above, but has two neopentylene methylphosphonate rings linked by one methylphosphonate unit (see structure below). At as low as 1 % P, a UL 94 V-2 rating can be achieved, and at 3 % P, a V-0 rating. Some volatility loss at processing temperatures is likely, but less than would occur with Antiblaze NT.



6.3 Polybutylene Terephthalate

This thermoplastic is commercially available on a large scale from many suppliers, and is growing rapidly. An authoritative review has been published by GE authors [37]. It has excellent processing, strength and chemical resistant properties and is used as a molding resin for such products as automobile and plumbing parts, housings and connectors for electrical equipment. Its fast crystallization which permits fast molding cycles is an outstanding feature. When glass fiber reinforced, it has improved tensile strength. The largest volume flame retardant use is electrical connectors. For electrical and electronic equipment in the US, it must often have a V-0 rating by UL 94. A review of flame retardancy of PBT by Green and Chung in 1990 shows the most advantageous additive at that time was a tris(dibromophenyl) phosphate which is no longer available, but useful data is given on other bromine additives [38].

6.3.1 Polymeric and Oligomeric Brominated Flame Retardants in PBT

A good balance of flame retardancy with good physical properties (although decreased melt flow) is achieved by use of a tetrabromobisphenol A polycarbonate resin added so as to have

about 11 % additive. Tetrabromobisphenol A carbonate has been used generally together with antimony trioxide. This carbonate is available in several varieties, Great Lakes (Chemtura) BC-52, BC-52HP and BC-58. These have the advantage of non-blooming, but they do have some tendency to degrade on heat aging. After exposure to a forced air oven at 180 °C for one week, the distortion temperature under load (DTUL) dropped by about 20 % with the polycarbonate additive.

These appear to have their origin in work at GE described in a number of patents from the 1970 era [39]. In most of these GE patents, a copolycarbonate of bisphenol A and tetrabromobisphenol A is used. It was also found at GE that transesterification between the polycarbonate and the PBT (which degrades physical properties) can be repressed by various additives such as a polyfluoroalkyl acid phosphate or a phosphoric acid-treated antimony trioxide [40] or phosphate salts [41].

It was found by GE that the level of tetrabromobisphenol A carbonate and Sb_2O_3 can be lowered while still passing the V-0 rating, by use of synergistic amounts of organically modified layered montmorillonite clay plus a small amount of dispersed tetrafluoroethylene [42]. Sometimes it is beneficial to have an Sb_2O_3 free formulation (Sb_2O_3 probably catalyses transesterification). In a GE patent it is suggested to use $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ as a synergistic co-additive, which provides long term thermal stability [43].

Glass-reinforced formulations of PBT with the tetrabromobisphenol A polycarbonate oligomer (end capped with tribromophenol) and antimony oxide can be rendered non-dripping by further addition of a few percent of a phosphonate salt such as calcium propanephosphonate according to a Lanxess patent [44]. A BASF patent application [45] shows the use of tetrabromobisphenol A polycarbonate in a blend of PBT and PET; a typical composition is 36.35 % PBT, 15 % PET, 12 % of the polycarbonate, 0.5 % pentaerythritol tetrastearate, 5 % Sb_2O_3 , 0.3 % potassium hydrogen tartrate (transesterification inhibitor), 0.5 % Blendex 449 (encapsulated PTFE) and 30 % chopped glass fibers. Further addition of 1–1.5 % polyamide 6/6.6 copolymer significantly improves gloss of the molded parts [46]. In another BASF patent application [47], a small amount such as 0.15 % of calcium acid phosphate is used as transesterification inhibitor.

For some time Great Lakes was offering brominated polyphenylene ether Firemaster® 935 [48], but probably discontinued it. The product is apparently still available in Japan from Daiichi as Pyroguard SR-460B [49].

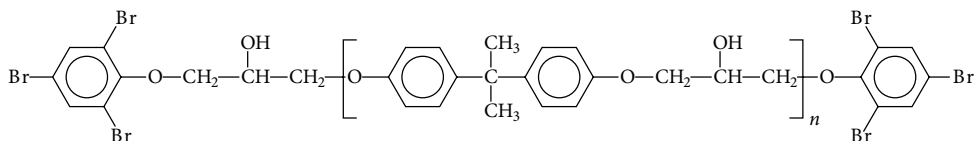
A high molecular weight brominated polystyrene such as Saytex® 7010 (or HP-7010) affords both good CTI performance and good thermal aging properties [50]. As a polymer with no vapor pressure, it is non-blooming. It is said to be outstanding on CTI performance, allowing about 300 V in glass-filled PBT, and shown to be substantially better in CTI than the brominated polystyrene oligomers such as Pyrochek® 68PB or Great Lakes (Chemtura) PDBS-80 [51, 52]. A later Albemarle patent application [53] suggests that a polybrominated anionic polystyrene may have advantages as a flame retardant additive for polyester fiber. Another Albemarle patent application [54] shows the use of brominated polystyrene in a PBT molding resin application; a typical formulation was 36.6 % PBT, 25 % glass fiber, 15 % brominated polystyrene (Saytex® HP-7010P), 12 % of an acrylic impact modifier, 5 % polypropylene (Novolen® 1100H), 6 % antimony trioxide and 0.4 % PTFE. Because Saytex HP-7010 has relatively poor melt flow characteristics, Albemarle is also offering a low molecular weight version

of similar material, HP-3010 [55]. Albemarle also sells a non-dusty masterbatch of brominated polystyrene in a polyester under the trade name Saytex® PBT 620.

Poly(pentabromobenzyl) acrylate (ICL-IP FR-1025) is also a non-blooming additive, but it is slightly less thermally stable and tends to lower the DTUL (distortion temperature under load) more than do the brominated polystyrene additives. On the other hand, it shows advantages in impact strength, CTI and melt flow in glass fiber reinforced PBT [56]. Its stability in thermal aging under recycling conditions is quite good; tensile strength is better retained than with non-flame-retarded PBT [57, 58]. Because FR-1025 is sensitive to laser irradiation it was suggested for laser marking formulation as described in a GE patent [59]. A recent Mitsubishi patent application [60] shows that flame retardant efficiency of FR-1025 with Sb_2O_3 can be improved if they are combined with talc, mica or kaolin. For example, a formulation providing a V-0 rating in the UL-94 test contains 6.7 wt. % FR-1025, 2.9 wt. % Sb_2O_3 , 2.0 wt. % talc and 0.5 wt. % PTFE.

Brominated epoxy oligomers and polymers of different molecular weight from 3 600 to 50 000 are available from ICL-IP as F-2000 series flame retardants. The polymeric flame retardants of this series show good flame retardant performance, non blooming behavior and high UV stability in PBT. Thermal stability improves with increasing molecular weight, however for better resin flow a lower molecular weight version is more preferable. Corrosion of processing equipment is a disadvantage of brominated epoxy oligomers, but this problem can be partially overcome with the use of acid scavengers and heat stabilizers [61].

Because epoxy oligomers of F-2000 series tend to adhere to the surface of processing equipment and potentially form black specks, ICL-IP introduced the F-3000 series [62] of epoxy oligomers with end capped tribromophenol groups (see structure below). The grade specifically recommended for PBT is F-3100 with molecular weight of about 10,000 [63, 64]. It has advantages particularly for use in glass-reinforced PBT having excellent thermal stability and non-adherence to metal surfaces. It also has good processing characteristics in compounding and injection molding, and is said to be particularly cost-effective for this application, although it also can be used in other thermoplastics. A recent patent to BASF shows [65] how melt flow can be further improved by using 1–1.5 wt. % superbranched polycarbonate in the formulation. Similar end capped brominated epoxy oligomers are also available in Japan from Sakamoto Yakuhi Kogyo as SR-T series [66].



Because most of the formulated FR PBT composites contain some amount of PTFE to suppress dripping, ICL-IP has developed a formulated flame retardant blend with built-in antidripping properties which is available as their SaFRon® 5500 series [67].

6.3.2 PBT with other Bromine-Containing Additives

In general, many aromatic bromine additives are suitable for glass-filled PBT, and typical levels of bromine are 8.2 % with antimony oxide, to achieve UL 94 V-0 at $\frac{1}{32}$ " thickness.

Antimony oxide is typically added at about 4–5 % as synergist. These formulations are usually free of blooming problems, but they may have processing difficulties (plate-out) and some color generation can be expected. Also, electrical properties (CTI) and thermal aging may be somewhat compromised.

Several non-melting bromine additives are also used, and have a melt-flow advantage. Decabromodiphenyl ether (oxide) ("decabrom", ICL-IP FR-1210, Albemarle Saytex® 102E, Chemtura DE83R) is in use and is priced favorably, although it has photostability limitations, and, being an insoluble particulate, lowers impact strength particularly in unreinforced PBT. Ethylenebis(tetrabromophthalimide) (Saytex® BT-93) is also used; it is more costly but does not discolor on light exposure as badly [68], and a specially purified grade Saytex® BT-93W is even better on light stability. In combination with some specific Cu compounds, Saytex BT-93 is suitable for laser printing formulations [69]. The thermal stability of BT-93/antimony oxide formulations permits good recyclability [70].

An alternative to the decabromodiphenyl oxide, with rather close properties but with less environmental concern, is Saytex® 8010, decabromodiphenylethane or possibly FR-245® (ICL-IP), 2,4,6-tris(2',4',6'-tribromophenoxy)-1,3,5-triazine. A recent Chinese study showed excellent non-blooming performance of FR-245 in glass-filled PBT compared to decabrom [71].

6.3.3 Polybutylene Terephthalate/Polycarbonate Blends

Blends of these two thermoplastics can have the solvent resistance of the semi-crystalline PBT with the good impact strength of the polycarbonate. The presence of polycarbonate also is favorable to flame retardance. Many brominated additives can be used, such as the tetrabromobisphenol A polycarbonate used in PBT itself. A recent patent application by a GE inventor suggests that a pentabromobenzyl acrylate polymer may be preferred, along with antimony oxide, a calcium phosphate interesterification-preventor, and a light-colored pigment such as titanium dioxide or zinc sulfide [72].

6.3.4 Non-Halogen Flame Retardant Polybutylene Terephthalate – Phosphorus Flame Retardant Additives

The loss of mechanical properties probably precludes the use of endothermic flame retardants such as ATH or magnesium hydroxide. Phosphorus-containing flame retardants do offer adequate performance.

The simplest formulation is 5–6 % red phosphorus (stabilized, coated), which can achieve a UL-94 V-0 rating at $\frac{1}{32}$ " PBT. Such a formulation might be used for a casing for electrical appliances [73]. The color of the additive may be a shortcoming for some applications, although a wide range of shades can be achieved by use of pigments. Good ventilation should be used in processing, but the evolution of traces of phosphine has been greatly reduced by stabilization and coating. However, the slow long-term evolution of phosphine and formation

of electroconductive and corrosive phosphorus acids on the surface of the plastic has caused some problems in the use of red phosphorus in electrical and electronic applications. The environmental toxicology appears quite favorable. Many synergistic combinations with red phosphorus are reported in the patent literature, which can help in tailoring some physical properties. For example, combination with zinc compounds (*e.g.*, zinc borate or stannate or zinc oxide) helps improve tracking index (CTI 600 V) [74]. Co-addition of melamine cyanurate helps with passing the Glow Wire Test (960 °C) [75].

In 2001, BASF introduced a phosphorus-flame-retarded PBT, Ultradur® B4400, containing no halogen, antimony or red phosphorus. With 25 % glass fiber, it meets UL 94 V-0 at 1.6 mm, glow wire ratings of 960 °C at 1 mm and has mechanical properties similar to the corresponding grades of halogen-containing PBT. This product has the advantages of lower density and higher electricals (600 V tracking resistance). The smoke density is lower than that of the halogenated grades, and the smoke toxicity is said to meet Airbus standards. The detailed formulation is not reported, but contemporary BASF patents show use of melamine cyanurate with phosphorus compounds; examples given are resorcinol bis(diphenyl phosphate), calcium hypophosphite and triphenylphosphine oxide [76, 77]. A combination of 15 wt.% calcium hypophosphite and 10 wt.% melamine cyanurate gives a V-0 rating in glass filled PBT [78]. A GE patent application [79] shows addition of 5 % triallyl isocyanurate gives improvement in physical properties.

Italmatch [80] has found that aluminum hypophosphite is an effective flame retardant for both unfilled and glass-reinforced PBT. In unfilled PBT, 12 % Phoslite® IP-A provides an oxygen index of 27 and a V-0 rating at 1.6 mm. In glass reinforced PBT, at 49.1 % PBT and 30 % glass, 20 % Phoslite IP-A gives V-0 at 1.6 mm. To obtain V-0 at 0.8 mm, a formulation of 54.1 % PBT, 25 % glass, 10 % Phoslite IP-A, 10 % melamine cyanurate suffices and also enables passing the glow wire ignition test at 775 °C.

Chemische Fabrik Budenheim has shown [81] that their novel long chain melamine polyphosphate (Budit® 3141) is an efficient flame retardant for PBT and PET. At 30 % loading in glass-reinforced PBT, it provides an oxygen index of 28 and a V-0 rating at 1.6 mm thickness. It also is effective in reducing smoke evolution.

Chinese studies [82] show that triphenyl phosphate plus melamine can enable a UL 94 V-0 rating and some evidence is adduced for a favorable interaction of these two additives. The volatility of triphenyl phosphate and melamine during processing could be a problem for this very inexpensive system.

6.3.5 Non-Halogen Flame Retardant Polybutylene Terephthalate – Phosphinate Salt Additives

BASF patents show a dialkylphosphinate salt (examples show calcium phosphinate but aluminum is mentioned) at levels of 10–20 % plus a nitrogen additive such as melamine polyphosphate at levels of 5–10 %, and some of the examples show admixture of PET with PBT [83]. Earlier patents to Clariant [84] and Ticona [85] show the use of aluminum diethylphosphinate in PBT, PET and blends. A later patent [86] to Lanxess shows flame retarding of PET-PBT blends using zinc diethylphosphinate plus melamine polyphosphate. These phosphinate salt additives are unusually effective compared to other phosphorus

additives. A recent study done in Germany showed that phosphinates tend to evaporate and provide a gas phase mechanism of action [87].

A Clariant patent application [88] shows the advantageous flame retardant use in PBT of an agglomerate of aluminum dialkylphosphinate with urea cyanurate and a small binder amount of polyvinyl alcohol. Other combinations claimed by Clariant [89] are the aluminum diethylphosphinate with a brominated polystyrene. Ticona [90] claims flame retardancy advantages in PBT for combinations of aluminum dialkylphosphinates with other phosphorus compounds, for example, aluminum methylethylphosphinate with resorcinol bis(diphenyl phosphate) and melamine cyanurate.

The grade of phosphinate salt (presumably aluminum diethylphosphinate) specially designed for polyesters is marketed by Clariant as Exolit® OP 1240. It is said [91] to provide a V-0 rating in glass filled PBT at loading levels of 15–22 wt. % and it can be applied alone or in combination with synergists like melamine cyanurate or melamine polyphosphate. Because of low specific gravity phosphinates provide advantages over brominated flame retardants in regard to polymer density and better electrical properties, *e.g.*, high tracking index (CTI = 500–600 V) [92]. Halogen-free grades of glass-filled PBT based on phosphinate technology are available from Ticona (USA) and Polyplastics (Japan) [93].

6.3.6 Non-Halogen Flame Retardant Polybutylene Terephthalate – Aromatic Phosphate Additives

Non-halogen PBT formulations from Du Pont show the use of combinations of melamine pyrophosphate (37 %) and an aryl phosphate oligomer such as RDP (mainly resorcinol bis(diphenyl phosphate)) (5 %). A UL 94 rating of V-0 at $\frac{1}{32}$ " could be reached with acceptable physical properties [94]. Since DuPont announced (2001) that they are offering non-halogen flame retardant PBT (in their Crastin® product group), it is possible that such formulations are commercial. In a study by Balabanovich [95] it was claimed by this academic worker that PBT could be flame retarded by tetraphenyl bisphenol A diphosphate, but results were only shown by oxygen index. By the more usual industrial test, UL 94, results have not been satisfactory.

Although not effective alone, combining an aromatic diphosphate with a novolac (char-former) enabled the achievement of acceptable flame retardancy by UL 94 criteria, as shown in an Akzo Nobel patent application [96]. For example, 15 phr Fyrolflex® RDP (resorcinol bis(diphenyl phosphate)), 10 phr novolac, and 0.5 phr PTFE in PBT gave a UL 94 V-0 rating at $\frac{1}{8}$ " thickness and no plate-out. A mechanistic study showed that aromatic bisphosphates (RDP or tetraphenyl bisphenol A diphosphate, BDP) interact with novolac and provide significant char enhancement compared to the system without novolac [97].

It is claimed in a recent Du Pont patent application [98] that inclusion of an alkaline earth salt such as calcium carbonate can better maintain the mechanical and electrical properties (such as CTI), presumably by neutralizing acid. For example, a PBT formulation of 38.7 % PBT, 29.0 % melamine pyrophosphate, 7 % Fyrolflex® RDP, 20.0 % glass fiber and 5.0 % calcium carbonate reaches a V-0 rating with a CTI of >350 V. Omitting the calcium carbonate, this CTI rating is not reached.

A non-halogen formulation for PBT and PET and blends thereof has been developed at General Electric in the Netherlands, to pass the glow wire test which is widely used in Europe for plastics in electrical equipment [99]. An example is given using 47.3 % PBT, 30 % glass fiber, 0.2 % antioxidant, 9 % RDP and 7 % melamine cyanurate, plus 6 % zinc sulfide to pass the 960 °C glow wire test at 1 mm thickness. Apparently, zinc borate or boron nitride, but not zinc oxide, can be substituted for the zinc sulfide. Pigmented formulations using BDP and melamine cyanurate to meet the glow wire test while retaining good ultraviolet light stability are shown in a later GE patent [100].

6.3.7 Non-Halogen Flame Retardant Polybutylene Terephthalate Using Melamine Cyanurate or Sulfate

A formulation of 60 % PBT, 40 % melamine cyanurate and 0.25 % pentaerythritol tetrastearate was shown in a DSM patent [101] to permit a UL 94 V-0 rating at 1.6 mm thickness. A BASF patent shows that melamine cyanurate (15 wt. %) in combination with volatile phosphorus compound (10–15 %wt.) like triphenyl phosphine oxide or triphenyl phosphine sulfide gives a V-0 rating in glass-filled PBT [102]. A combination of melamine cyanurate (9 wt. %) in combination with melamine polyphosphate (15 wt. %) was shown to give V-0 rating in unfilled PBT [103].

Dimelamine sulfate, at 25 phr in PBT, is shown in a Polyplastics patent to allow a V-2 rating [104].

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7 Flame Retardants in Commercial Use or Advanced Development in Polycarbonates and Polycarbonate Blends

7.1 Introduction

This chapter deals only with the commercial aspects of polycarbonates and their principal blends. Another publication by the present authors discussed the decomposition of polycarbonates and their flame retardancy chemistry from a more basic point of view and also covered a wider range of publications and patents, whether commercially applied or not [1]. A brief review of the applied aspects of flame retardant polycarbonates has been published by the present authors [2] (the present chapter is an update of this review) and by Innes [3, 4]. The commercial polycarbonates of importance are derived from bisphenol A by reaction with phosgene or by transesterification with diphenyl carbonate. There are also copolycondensed resins with polycarbonate and polyester components. The original producer was Bayer followed in the 1970s by General Electric under the trade name of "Lexan". There are now over ten producers of polycarbonates.

Polycarbonates are substantially amorphous polymers characterized by good hardness, stiffness and outstanding impact strength, with notched Izod impacts typically around 15 ft-lb./in. The good impact is retained at low temperatures, even as low as -100°C . Other features are glass-like transparency, dimensional stability, and thermal stability, allowing for service temperatures up to about 140°C . The glass transition temperature is about $140\text{--}150^{\circ}\text{C}$ [5] and heat distortion temperature of about $132\text{--}8^{\circ}\text{C}$. Weaknesses include rather poor chemical resistance and stress cracking.

Polycarbonates are widely used in automotive, rail and aircraft, office equipment, electronic devices, batteries, data recording media, medical equipment, and glazing. They may be injection molded, extruded to make rods, profiles or sheets, or blow molded to make bottles and packing films. The annual volume of polycarbonates is believed to exceed three million metric tons.

Compared to other types of polyesters, polycarbonates are relatively easy to render flame retardant by virtue of their low heat of combustion and their propensity to foam and char when exposed to fire. The oxygen index of the typical bisphenol A polycarbonate without flame retardants, is about 25 and its UL 94 rating is typically V-2. The heat of combustion is $31\text{--}32\text{ kJ/g}$ which is much less than a typical styrenic polymer ($43\text{--}44\text{ kJ/g}$) [6]. The char yield under standard TGA conditions under nitrogen is $22\text{--}29\%$. Most polycarbonate film grades have a rating of UL94 V-2 at 375 microns and above, and thicker thermoformed or extruded sheets or profiles generally meet V-2 without any flame retardant additive. Minimally, non-flame-retarded polycarbonates (extruded profiles, or sheets used in laminates)

are at least UL 94 HB rating. Polycarbonate used in automobile interiors such as instrument panels quite likely can meet MVSS 302 without flame retardants.

7.2 Bromine-Based Flame Retardancy

An early additive, still used commercially, is a carbonate oligomer of tetrabromobisphenol A, made by Chemtura as BC-52 (phenoxy-terminated, formula weight ~ 2500 , 51.3 % Br) and BC-58 (brominated phenoxy-terminated, formula weight $\sim 3\,500$, 58.7 % Br). Originally, there was some patent-related difference between these. Now, they are substantially used in the same way, at about the 8–10 % additive level (an early patent shows 14 % [7]), which can provide a V-0 rating at $\frac{1}{16}$ " thickness. An analog of BC-58 is also available in Japan from Teijin Chemicals under the trade name FG8500. These oligomers are non-blooming but can somewhat impair impact and light stability. BC-52 allows better transparency than does BC-58. On the other hand, BC-58, which can be used at a somewhat lower additive level, is slightly better in regard to retention of impact strength, and may have a cost/effectiveness advantage. A study was done at FMC on the effect of a brominated polycarbonate additive, showing an effect mainly on tensile stiffness, not on processability [8, 9]. Bromine-containing polycarbonates can encounter iron-catalyzed decomposition and some corrosion of steel, necessitating special steel alloys [10].

Epoxy oligomers made from tetrabromobisphenol A by ICL-IP have been used in polycarbonate. Two grades of brominated epoxies F-2100 and F-2300H with molecular weight above 20 000 are specifically recommended for PC/ABS. This type of additive may somewhat lower heat distortion temperature but shows a positive effect on impact strength [11]. About 6–9 % of this polymer can improve melt flow and thus facilitate the molding of thin-walled parts [12]. Recently ICL-IP introduced SaFRon 5531 which is a formulated system based on brominated epoxy oligomers which contain an antidrip component [13–15]. The flame retardant performance of SaFRon 5531 in polycarbonate in comparison with decabromodiphenyl ether ("Deca") and in PC/ABS in comparison with resorcinol bis(diphenyl phosphate) (RDP) (see below) is shown in Table 7.1.

Tetrabromobisphenol A can also be reacted into the polycarbonate during its production at about the 3–5 % bromine level to obtain a V-0 rated material [16]. General Electric also manufactured a co-polymer of bisphenol A and tetrabromobisphenol A terminated with tribromophenol under the developmental nomenclature PC105B [17]. In order to adjust bromine content, BC-58 can be added. A similar co-polymer was produced by Idemitsu [18]. With about 10 wt. % of tetrabromobisphenol A and 3 wt. % tribromophenol units in the structure it produced a UL 94 V-0 rating.

Other brominated additives have been used. Chemtura suggests that the compounder must find a balance of required additive level vs. processability, effect on physical properties, especially impact, and cost. Solid flame retardant additives which do not dissolve in the plastic reduce impact quite seriously. Poly(dibromostyrene) (Chemtura PDBS-10 or PDBS-80 which has better flow) is effective and non-blooming. A typical loading is 7–10 %. A higher molecular weight brominated polystyrene (PBS-64HW) is also effective. A relatively new stable

Table 7.1 Flame Retardant Performance and Physical Properties of SaFRon 5531

Resin type	Polycarbonate			PC/ABS alloys (85/15)	
FR system	Deca DPO	SaFRon-5531		RDP	SaFRon-5531
Composition, wt. %					
Resin	95.6	92.9	77.9	91.3	93
Glass fiber	—	—	15		
FR system	4.4	7.1	7.1	8.7	7
Properties					
Flame retardancy, UL 94, (1.6 mm)	V-0	V-0	V-0	V-0	V-0
MFI, g/10 min (PC 300 °C — 0.2 kg and PC/ABS 240 °C — 5 kg)	19	16	10	7	4
Tensile properties					
Strength at yield, MPa	66	64	na	63	55
Elongation at break, %	56	101	na	65	136
Modulus, MPa	2300	2200	na	2500	2400
Izod notched, J/m	105	745	756	630	653
HDT, °C	118	123	138	90	116

polybrominated polystyrene is available as Albemarle Saytex® 3010. These dissolve in the PC and do not hurt impact.

Decabromodiphenyl ether (several suppliers) can be used and has a likely price advantage. In some European and Far Eastern markets, there is a diffuse concern about polybrominated diphenyl ethers as a class. A newer non-diphenyl ether product which has somewhat similar performance properties is 1,2-bis(pentabromophenyl)ethane (Albemarle's Saytex® 8010 or Chemtura Firemaster® 2100). A lower cost brominated additive such as Chemtura FF-680 (1,2-bis(tribromophenoxy)ethane) can be used but a blooming problem is possible. Polybrominated trimethylphenylindane (ICL-IP's FR-1808) is an effective flame retardant, compatible with PC which can remain transparent upon addition of 15–40 % of the additive [19]. This product is not offered commercially now.

Antimony oxide is not usually needed in polycarbonate halogen-based formulations, and in fact is generally to be avoided in polycarbonate because its slight residual acidity causes some loss of molecular weight during processing, and it causes opacity unless the relatively expensive ultra-fine Sb₂O₅ is used. The exception is in glass-filled PC where the glass makes up for any strength loss caused by the antimony oxide.

7.3 Anti-Dripping Additives

Fibrillated finely-divided polytetrafluoroethylene (PTFE) is often added in less than 0.1 % amounts to retard dripping during the UL 94 test. Practical and performance advantages

can result from a highly uniform PTFE addition process by the polycarbonate manufacturer [20, 21]. Interestingly, Asahi Kasei found that PTFE works well as an antidripping agent only if fibrils form in the resin some kind of branched or cross-linked structure which can be observed in the microscope [22]. Bayer has a proprietary method of blending an aqueous PTFE dispersion into the polycarbonate and then drying the mixture [23]. The use of PTFE does favor opacity. Opaque formulations using the sulfonate salt plus antidrip agent are said to be able to reach an M-1 classification by the French epiradiateur test but also a satisfactory rating by the Federal Aviation test FAR 25-853ab which is relevant to the aircraft application [24].

High molecular weight PTFE able to form fibrils is not flowable at room temperature, but needs to be cooled down below 19 °C [25]. This creates certain problems for processing, which can be avoided if PTFE is imbedded into SAN during emulsion polymerization of SAN [26]. Alternatively PTFE can be coated with polystyrene followed by polyacrylonitrile [27]. Recently, 3M developed PTFE grade Dyneon® TI MM 5935 EF which is free-flowable and it is said not to undergo premature fibrillation which results in better dispersion and higher efficiency [25, 28].

Burning drips can also be reduced by the use of a branched (and thus higher melt-viscosity) polycarbonate, and by various silica-based additives. Some recent GE patents suggest that improved fire resistance and drip resistance can be achieved by small percentages of an elastomer-modified graft copolymer and a polysiloxane-polycarbonate copolymer [20]. Usually branched polysiloxanes are used in combination with sulfonic acid alkali salts to produce transparent V-0 grade polycarbonate. This will be discussed later in this chapter.

7.4 Non-Halogen Flame Retardancy – General Comments

Particularly in the electrical and electronics industry, and particularly in Europe and the Far East, there has been a demand for non-halogen flame retardant plastics. This stems from a combination of “green” marketing strategies and costs created by regulations particularly in regard to electrical and electronic waste disposal.

7.4.1 Phosphates

Aromatic phosphate ester additives have limited use in unblended (neat) PC because of an adverse effect on thermal and hydrolytic resistance. Some of the lower molecular weight phosphates such as triphenyl phosphate and alkylphenyl diphenyl phosphates have a tendency to “juicing” at high temperature, *i. e.*, migrating to the surface where they cause deposition on the mold and sometimes surface cracking. The oligomeric or diphosphates such as resorcinol bis(diphenyl phosphate) (RDP) or bisphenol A bis(diphenyl phosphate) (BDP) are preferred from the standpoint of non-juicing. These additives are the leading products for use in PC-ABS blends (discussed below) but their use in unblended PC is relatively small. Sterically hindered diphosphates are preferred for unblended PC because of high hydrolytic stability [29]. One of this diphosphates tetrakis(2,6-dimethylphenyl) resorcinol diphosphate, available from Daihachi as PX-200 gives a V-0 rating in PC at 9 wt. % loading.

A Japanese patent to Sumitomo Dow indicates that diphosphates may be most useful in combination with a silicone [30]. Likewise, a Bayer patent applications [31, 32] suggest the use of the phosphorus flame retardants in a PC blended with a graft polymer containing silicone or silicone acrylate structures, together with a small amount of a borate, to achieve both flame retardancy and good impact. A recent GE patent shows the use of 10–12 wt. % BDP with 2.5 wt. % of a polycarbonate-polydimethylsiloxane copolymer to give a V-0 rating in polycarbonate [33]. Interestingly, it was shown that only 1 wt. % BDP with 1 wt. % low melting glass can provide a V-0 rating in PC [34]. Flame retardant performance is not lost even after three re-extrusions.

7.4.2 Other Phosphorus Compounds

It has been found by Italmatch [35] that a polycarbonate can be efficiently flame retarded to a V-0 rating with a hypophosphorous acid calcium or aluminum salt. It is advantageous to include a phosphate ester such as triphenyl phosphate, resorcinol bis(diphenyl phosphate) (RDP), or bisphenol A bis(diphenyl phosphate) (BDP), and small amounts of PTFE.

Although the phosphazenes have been much studied, their commercialization as flame retardants seems limited only to Japan. A study by Sato at an electronics group in Kyoto [36] showed that polycarbonates with 0.5–20 parts of a phosphazene, especially a phenoxy-substituted cyclic, linear or crosslinked phosphazene, plus 0.01–3 parts of a synergistic phenyl methyl siloxane, and 0.01–2 parts of an potassium sulfonate (see below) provided good flame retardancy together with good impact and resistance to heat and light.

7.4.3 Sulfonate Salts

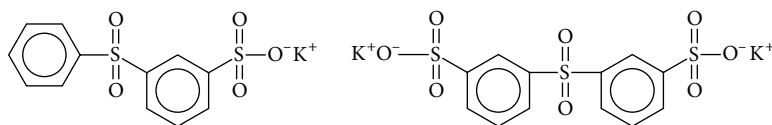
Polycarbonates can be flame retarded with very low levels, well below 1 %, of various sulfonate salts [3], now widely used by a number of manufacturers and compounders. Generally the resultant flame retardant grades will meet V-0 at $\frac{1}{16}$ " if unfilled, but if glass-filled, the thickness may have to be greater to meet V-0. A sulfonate-containing polycarbonate should be further processed very carefully, because any overheating can cause decomposition and loss of physical properties.

The first discovery appears to have been at Bayer, where sodium or potassium salts of perfluoroalkylsulfonic acids were found effective in amounts well under 0.1 %, allowing clear formulations [37]. Bayer has been selling flame retardant grades of polycarbonates containing this type of sulfonate, presumably potassium perfluorobutanesulfonate, for many years.

Subsequently, it was found that aromatic sulfonate salts with electron-withdrawing substituents on the ring, such as halogens or arylsulfonyl were also effective, and these systems have been the subject of many patents [38].

One of the more successful sulfonates for this application, judging by numerous flame-retardant polycarbonate patents citing it, is the potassium salt of diphenyl sulfone mono- and disulfonate (KSS), made in the UK by Seal Sands Ltd. and in the US by Arichem LLC (formerly by Sloss Industries). It allows for transparent or translucent formulations. The Sloss product is said to have minimum 60 % monosulfonate and maximum 28 % disulfonate (see chemical structures below). Sloss Industries also offers sodium trichlorobenzenesulfonate (STB-FR)

for this application, particularly for opaque formulations. With either of these additives in the range of 0.1–0.5 %, a UL 94 V-0 rating at 3.2 mm thickness can usually be obtained. Drip suppressants such as PTFE are used when transparency is not required, or a silicon-based type such as polyphenyl methyl siloxane when transparency must be retained. Formulations in which opacity is acceptable can utilize, for example, 0.5 % STB-FR and 0.1 % PTFE to meet the V-0 requirement at 3.2 mm thickness of polycarbonate.



These sulfonate salts are particularly effective in polycarbonates in combination with halogenated additives [39] such as a tetrabromobisphenol A/bisphenol A polycarbonate, which permits lower smoke and lower heat release. Low total cost can often be attained by use of a combination of sodium trichlorobenzenesulfonate and a brominated polycarbonate additive. With STB-FR as sole flame retardant, the halogen content can be low enough that the formulation is considered non-halogen by some regulatory classifications [40].

Combinations of these sulfonate salts with soluble bromine additives and the choice of a branched polycarbonate can allow transparent formulations to reach a V-0 rating at 0.8 mm. Generally the use of the bromine additive is also needed to pass the glowing wire test at 960 °C/5 s or to get an M3 rating in the French epiradiateur test [10].

Patented combinations of the sulfonate salts with a variety of other synergists and co-additives are numerous and are reviewed in our recent published review [1]. A notable recent patent to General Electric shows substantially improved results in a glass-filled polycarbonate (expressed by higher probability of a “first time pass” in a modified UL 94 test) by co-addition of a very small amount of phosphorous acid [41]. The best rating is shown by adding 0.015 phr potassium perfluorobutanesulfonate, 0.015 phr sodium toluenesulfonate and 0.0963 phr phosphorous acid. Another GE patent shows combination of perfluorobutanesulfonate, phosphorous acid and deionized water [42]. The actual commercial use of these combinations is difficult to ascertain but seems likely.

Ciba [43] has claimed the flame retarding of PC with extremely low levels of certain sulfonated triazinylaminostilbenes and sulfonated benzotriazolylphenols. Related alkali metal salts of sulfonamides and sulfonimides [44–46] are described as flame retardants for modified polycarbonates and possibly such additives are in use. Sodium or potassium polystyrenesulfonates are also shown in patent literature [47, 48], which apparently allow recycling flame retardant polycarbonate. Sulfo-modified polyesters made from 5-Na-sulfoisophthalic acid and available from Eastman as 38S and 55S were recently shown in Bayer patent application [49] being efficient in polycarbonate at 0.1 wt. % loading. Similarly, polyphenylene ether oligomers with Na or K sulfonate chain ends give V-0 in polycarbonate at 0.3 wt. % loading [50].

Most recently the potassium perfluorobutanesulfonate, formerly made captively by Bayer, has been marketed by 3M as FR-2025 in the U.S. for this application, the original patents having expired. There also appear to be Japanese manufacturers [51, 52]. One of the Japanese sulfonate products is reported to contain a silicone component and a lactone processing aid

[53]. An important advantage of potassium perfluorobutanesulfonate is that it can provide a V-0 rating in polycarbonate at as low of 0.06–0.08 % by weight, and can allow an optically clear, haze-free grade of polycarbonate for extrusion and molding. The pricing is such that the added cost/lb. of resin is similar or slightly lower at 0.08 % addition level to a typical brominated flame retardant at the 5–10 % level. A recent GE patent application [54] claims that the use of lithium perfluorobutanesulfonate as the PC flame retardant affords good transparency. A series of more recent patents show synergistic combinations of the sulfonate salts [55, 56]. A GE patent states that the borderline reliability of obtaining a V-0 rating using the potassium perfluorosulfonate by itself, and shows a better result by combination with sodium toluenesulfonate [57]. Other GE patents, both old and new, show siloxane combinations with a sulfonate salt [58–60]. Japanese companies also have patents showing this type of combination [61]. Such combinations are probably in use.

Most of the favorable examples of sulfonate salts as flame retardants are with polycarbonates, and indeed, mechanism studies suggested that their extremely efficient activity might be specific to polycarbonates [62]. At levels of as low as 0.2 %, the sulfonates seemed to accelerate carbon dioxide evolution and the breakdown of the polymer to fragments, thence to a somewhat intumescent char [63–65]. In a later Japanese study, the mode of action of the various effective sulfonates was confirmed to be a catalytic effect (noting that the effective salts are those of strong acids) on the route and rate of decomposition; these researchers did not find char formation to be a dominant factor but they noted that enhanced cleavage at the isopropylidene group seemed important [66]. Another study by these researchers confirmed that heavier alkali metals like K or Cs show a stronger effect compared to Li or Na [67]. A further factor which affects efficiency is a good match of the temperature of thermal decomposition of the salt and polycarbonate. A Chinese study found that the sulfonates accelerated thermodegradation and the different sulfonates caused different final stages [68]. At the same time surprisingly it was noted that metal sulfonates increase the activation energy of decomposition of polycarbonate [69].

The sulfonates are effective not only in unfilled polycarbonates but also in glass-fiber-filled formulations, and it is said that the stringent UL 94 5V rating can be reached in such filled systems [10]. A recent Teijin patent application [70] shows potassium perfluorobutanesulfonate (KPFBS) with a low content of F^- ion in combination with phenylsiloxane having free SiH groups being effective in glass-filled PC. If F^- content exceeds 10 ppm the polymer drips and loses the V-0 rating. As low as 0.01 wt. % potassium perfluorosulfonate combined with 0.1 wt. % toluenesulfonic acid and 0.2 wt. % PTFE provide a V-0 rating in glass-or mineral-filled PC (ca. 10 % filler) [71].

The sulfonates are said to not be effective in ABS-PC blends [66, 72]. However, a patent to Mitsubishi Engineering Plastics shows that up to 20 parts of a diene-containing multi-layered polymer can be present per 100 parts of polycarbonate in a sulfonate-retarded system [73]. Also, a recent GE patent shows this sort of blend with a flame retardant amount of an alkylbenzenesulfonate [74]. Preparation of sulfonated ABS by reacting with sulfuric anhydride and then neutralizing with KOH is shown in a Sony patent application [75]. The resulting ionomer contains about 14 wt. % sulfur. At 0.5 wt. % addition level in combination with 0.1 wt. % PTFE it provides V-0 in PC/ABS (9 : 1).

7.4.4 Other Salts

A Ciba patent application [76] discloses the use of an aromatic phosphoric acid ester salt, exemplified by Irgastab® NA 11 (sodium salt of a cyclic methylenebis[2,4-di-*tert*-butylphenol] phosphate, a nucleating agent for polypropylene), as a flame retardant for PC which allows transparency and preserves the other good mechanical and thermal properties. Bayer in their patent [77] suggested use of the magnesium salt of diphenyl phosphoric acid as a flame retardant for PC/ABS. An Asahi Denka patent application [78] shows a very broad range of metal organophosphate salts which are used at 0.1–0.2 wt. % level as synergistic co-additives to aromatic bisphosphates.

7.4.5 Silicone-Based Systems

In addition to the silicone synergist systems mentioned above in the sulfonate discussion, recent development of a unique silicone-alone system was described by NEC Corp. (Japan) [79, 80]. This utilizes a special silicone with a branched chain structure, a phenyl-rich mixture of phenyls and methyls in the chain, and methyl groups as termini available from Shin-Etsu [81] and probably from Dow Corning [82]. This silicone is said to not adversely affect strength, moldability and heat resistance; impact is said to be better than that of polycarbonate containing a bromine-based flame retardant [83]. This product is probably in commercial development. The system is said to work in polycarbonate blends as well. Combination of the branched polysiloxane with only 3 wt. % aromatic bisphosphate provides V-0 rating in PC/ABS blend of 95:5 [84].

It has been proposed that this silicone migrates to the surface of a polycarbonate during molding [79, 83] and in fact TEM images of molded PC confirmed this [85]. However recent work done by another Japanese research group [86] showed that these branched siloxanes actually react with polycarbonate during decomposition in the bulk of the polymer and build up in the char structure.

Interesting work was done by researchers at Asahi Chemical Industries [87] using silicones with linear and branched structures as well as silicones with different content of phenyl and methyl groups. Their conclusions were different from NEC observations, *e. g.*, they found that linear silicones are more effective than branched, because they migrate faster to the surface, and silicones with higher content of methyl groups are more effective because they are richer in Si.

Phenyl-substituted siloxanes are disclosed in Cheil (Korean) applications [88] as flame retardants in TiO₂ pigmented impact-modified PC and these formulations are said to have good light reflectance. Ethylphenyl [89] or isopropylphenyl [90] branched siloxanes behave very similarly to methyl phenyl siloxanes.

7.5 Polycarbonate-ABS Blends

Blends of polycarbonate with various styrenic polymers such as SBS or SAN are available, but the principal such blend is with ABS.

In these commercially important blends, the PC contributes impact and heat distortion resistance, while the ABS contributes processability, chemical resistance, and cost reduction below that of pure PC. Blends of this sort also retain impact toughness with age better than does plain PC. The styrenic component of these blends causes high smoke evolution, but this is not a criterion in most of the applications of these blends.

PC-ABS blends are used for equipment housing, and structural parts requiring stiffness, gloss, impact and heat resistance higher than ABS, but requiring costs below polycarbonate. Housings requiring UL V0, but not 5VA, for example in portable electronic devices such as laptops are typical applications for PC-ABS. Other uses include housings requiring long term resistance to discoloration under UV light such as computers and printers. Other typical uses include automotive interior parts (instrument panels, ventilation ports, lamp covers) some of which must function at 100–125 °C and require good ductility during manufacturing. Materials in the passenger compartment of the automobile must pass the Federal MVSS 302, a fairly lenient maximum rate of horizontal burn requirement. Because of good electrical insulating properties, these blends are also used for electrical sockets and plugs, where they should be UL 94 V-0 rated. Typical flame retardant blends in the U.S. have 85 % polycarbonate and 15 % ABS although a wide range of proportions, even some predominating in ABS, can be found on the world market. These two thermoplastics show good miscibility of the two individual components. Where flame retardancy is not required, the ABS content is often higher, 30–40 % being typical.

General Electric researchers [91] have developed statistical tools to be applied to UL 94 test results to arrive at optimized formulations having reliable V-0 and 5V ratings for PC-ABS.

7.5.1 Halogen Additives in PC Blends

Polybrominated epoxy resins are compatible with the blends, helping flexural strength but compromising impact if reactive epoxy groups are present [92, 93]. High molecular weight epoxy polymers with tribromophenol endcapped groups, available from ICL-IP, are used without antimony trioxide in PC-ABS. They provide high HDT (close to non flame retardant resin) and good impact properties [94]. ICL-IP also offers a formulated package with antidripping agent under the tradename SaFRon 5531 [13–15] (see Table 7.1). The tetrabromobisphenol A polycarbonate oligomer, used in pure PC, has less compatibility with the usual PC-ABS blends [95].

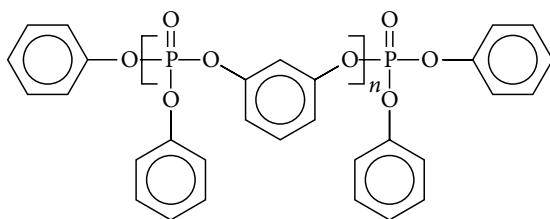
7.5.2 Phosphorus Compounds in Blends of Polycarbonates and ABS

These blends respond well to phosphate flame retardants, and this fact has strongly favored their commercial usage in electrical and electronic equipment. At 10 % triphenyl phosphate, a V-0 rating can be obtained provided that the formulation also contains a small amount of an antidrip agent such as polytetrafluoroethylene (0.3 % at most) [96]. Triphenyl phosphate is probably the most cost-effective of the phosphate ester additives, typically being effective at 10–18 %. Because of its low melting point, it can cause bridging in the feeding equipment, and volatility loss during extrusion and molding. Volatility during normal use in electronic

plastics is minimal but has elicited some environmental concerns despite very low level of detection in air [97, 98].

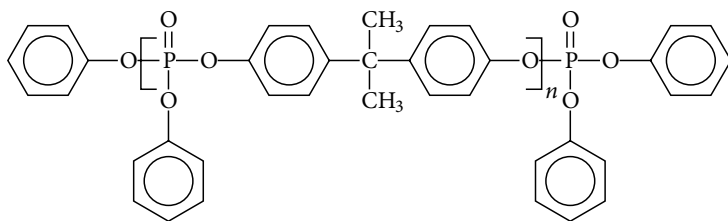
Tert-butylphenyl diphenyl phosphate has advantages for this application because it is liquid (easier for mechanical feed to mixing equipment), better retention and better hydrolytic stability, however, like all the triaryl phosphates, it still causes exudation (“juicing”) [99]. Tert-butylphenyl diphenyl phosphate shows better stress cracking resistance compared to triphenyl phosphate [99, 100]. Cresyldiphenyl phosphate [96] or tricresyl phosphate [101] or trixylenyl phosphate [102] are also mentioned in patent literature, but their actual use is not clear. To avoid the exudation problem, higher molecular weight di- and oligomeric phosphates are used. Some phenyl phosphorodiamidates are also said to show a good balance of fire retardance and other properties [103] but their actual use is not known to the present authors.

One effective commercial product is an oligomeric mixture mainly resorcinol bis(diphenyl phosphate) (ICL-IP’s Fyrolflex® RDP, Chemtura’s Reofos® RDP, Daihachi’s CR-733S and Asahi Denka’s ADKStab® PFR, see structure below). This product is actually a mixture of oligomers up to about five phosphate groups but mostly the diphosphate. This is mainly used in PC-ABS blends and in PPO-HIPS blends. It has higher percentage P (10.8) than the monophosphates and, in a commercial PC-ABS blend with 25 % or less ABS, it can be used at about 8–12 % loading to obtain a V-0 rating with co-addition of a small amount (< 0.3 %) of PTFE to retard dripping. RDP shows good thermal stability and low volatility during processing. Moreover, it acts as a processing aid in PC-ABS blends [104]. A GE patent, probably covering a commercial product, claims flame retardant blends of a polycarbonate, a styrenic copolymer and oligomers of the RDP type where there are 2.2 to 2.7 phosphate units in the oligomer [105].

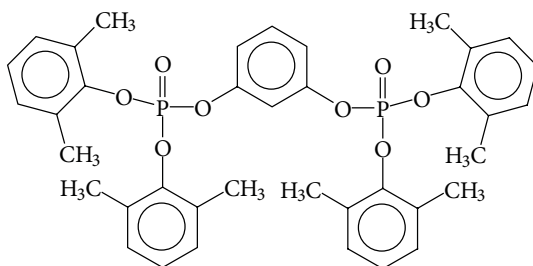


RDP does show some hydrolytic instability on aging which is deleterious to the acid-sensitive PC particularly in recycling. With care, PC-ABS containing phosphate flame retardants can be recycled as discussed by Moy [106]. Improved stability of the formulation is achieved by addition of acid scavengers such as epoxies [107, 108], hydrotalcite [109], oxetanes [109], orthoesters or MgO (which can be a residual amount from the use of a MgCl_2 catalyst in making the phosphate) [110]. Other inorganic additives such as zeolite [111], talc [112, 113] or dispersed silica [114] also seem to help high temperature dimensional stability. Finely divided organoclays can also reduce afterflame time [115]. Polymer-modified layered silicate minerals can also provide reduced decomposition rates in case of fire, as disclosed in a Bayer patent application [116]. GE researchers disclose the advantage of using vinylsilane surface treated siliceous fillers [117].

Another successful phosphorus additive for PC-ABS is bisphenol A bis(diphenyl phosphate) with higher oligomers and small amounts of triphenyl phosphate [118]. This product is available from three US manufacturers, as ICL-IP's Fyrolflex® BDP, Chemtura's Reofos® BAPP and Albemarle's N-CendX® P-30. It is also available from Japan as Asahi Denka's FP-700 and Daihachi's CR-741 (see structure below). It has slightly lower percentage P (8.9) and about 10–15 wt. % is needed for V-0 rating depending on PC/ABS formulation. It is significantly more viscous than RDP and thus somewhat more difficult to handle. It has distinctly better hydrolytic stability than RDP, and somewhat better thermal stability [119]. The long term hydrolytic stability [120] can be further improved by the same kind of additives mentioned in regard to RDP. Addition of a fibrous mineral such as wollastonite [121], or a highly charring phenoxy resin [122] to a formulation of BDP in PC-ABS improves impact and reduces afterflame time.



Another hydrolysis-resistant diphosphate useful for this application, but probably more costly, is tetrakis(2,6-dimethylphenyl) 1,3-phenylene diphosphate (Daihachi PX-200® and Asahi Denka's FP-500, see structure below) [123–125]. This solid product, because of the steric hindrance of the 2,6-dimethylphenyl groups, has substantially higher hydrolytic stability than RDP. It is effective in providing a V-0 rating to PC-ABS at 12–16 % loading.



It was found that a combination of RDP or BDP with triphenyl phosphate or with tert-butylphenyl diphenyl phosphate [126–129] or even a combination of RDP with BDP [130] provides an efficiency advantage; such combinations can allow loadings as low as 10 % still reaching the V-0 rating. This is probably related to a combination of vapor phase (flame zone) action and condensed phase action [131]. It was shown by a German research group [132] that triphenyl phosphate has mostly vapor action, RDP mainly vapor but some condensed phase action, and BDP has an important condensed phase action with some vapor phase action.

Many variations on the above-described aryl phosphate structures are described in the patent literature, but are not known to have been commercially used or developed for PC or PC blends. The full range of these structures is reviewed by us elsewhere [1].

The phosphate flame retardant PC-ABS can also be enhanced by inclusion of several percent of a polyphenylene ether which may be maleic anhydride grafted [133].

The flame retardant mode of action of tetraphenyl resorcinol diphosphate (and probably the above-described related structures) in PC-ABS blend appears to involve the PC undergoing a rearrangement to a phenolic polymer which then is phosphorylated, the end result being the accumulation of a phosphorus-containing char barrier [134]. There is a more detailed discussion of the mechanism of action in our review [1]. Recent studies of the mechanism of action of aromatic phosphates in PC-ABS were published by German researchers [132, 135]. High PC-low ABS blends flame retarded by resorcinol bis(diphenyl phosphate) (RDP) or other aryl phosphates are afforded shorter burning times under UL 94 V conditions by the addition of nanometer-sized inorganic compounds exemplified by Al_2O_3 , TiO_2 , boehmite, zeolites or other aluminosilicates as shown in Bayer patents which probably have found commercial practice as nanocomposites [136, 137].

PC-ABS blends flame retarded by about 10 % of a bisphenol A oligophosphate (BDP) were further enhanced at Bayer [138] by the addition of about 5 % of a layered silicate (sodium montmorillonite) converted to a nano-clay by treatment with a polyethylene glycol monomethyl ether.

7.5.3 Other Phosphorus Compounds in PC-ABS Blends

Cyclic phenoxy-substituted phosphazenes which are usually synthesized as a mixture of six- and eight-membered rings with some linear oligomers were found to be efficient in PC-ABS at 12–15 wt. % [139]. The phenoxyphosphazenes are synergistic with RDP or TPP [140]. These phosphazenes are produced in Japan by Otsuka. Because of their symmetrical structure (low or zero dipole moment) they have good electrical properties. It is believed that the main use of these phosphazenes is in battery cases.

Recently Otsuka researches were involved in development of bisphenol- or phenylene-bridged or partially cross-linked phosphazenes [141]. Some of these materials were tested by Cheil [142, 143] in PC-ABS, in combination with TPP, RDP or BDP. The advantage is said to be a good balance of flame retardancy and other properties.

7.5.4 Other Flame Retardant Systems for PC-ABS Blends

Fuji Xerox [144] has shown that PC, PC-silicone copolymers and blends with ABS can be flame retarded with metal hydroxides such as magnesium hydroxide in the size range of 1–500 nm which is coated with a silicone, plus a flame retardant auxiliary such as zinc borate. Earlier these researchers found [145] that mixed aluminum magnesium hydroxide can provide a V-0 rating in PC at only 5 wt. % loading level.

7.6 Polycarbonate-Polyester Blends

Blends of PC with thermoplastic polyesters, particularly with PET, are commercially used especially in the automotive industry because of their good weatherability and hydrocarbon solvent resistance. Where flame resistance is required, the systems rather similar to those used in PC-ABS. RDP and BDP are quite effective; for instance, only 4 % RDP is needed in PC-PET (5 : 1 w/w) to pass V-0. Because both PC and PET are acid-sensitive, better long term stability results are likely to be obtained with the more hydrolytically stable diphosphates. Epoxy stabilizers can be used as well [146, 147].

Blends of polycarbonate and thermoplastic polyester have been made flame retardant with a good balance of mechanical and processing properties, according to a Bayer patent application [148], by a combination of BDP and a pentabromobenzyl acrylate polymer (ICL's FR-1025). Physical properties of blends flame retarded with aromatic bisphosphates can be further improved by addition of 0.5 wt. % mica and 0.1 wt. % talc [149].

7.7 Other Polycarbonate Copolymers and Blends

GE (now SABIC) has a series of patent applications [150–152] on new polycarbonates with, instead of or in addition to the usual bisphenol A unit, have a cyclohexylidene bridge between the rings, which are also *o*-methyl-substituted. These are said to maintain the good response to the usual polycarbonate flame retardants plus having improved flow, impact and scratch resistance. Some are compounded with one or more impact modifiers, silicones and antidi-pping agents.

GE has published patent applications on polycarbonate-polysiloxane copolymers and various blends with further polycarbonate [117], impact modifiers and polyether-polyimides [153]. Some of these blends, such as the ones with polyether-polyimides have exceptionally low smoke, as well as being flame retarded by the usual additives. GE patent applications [154, 155] show that blends of polycarbonates with polysiloxane-polycarbonate copolymers, impact modifier polymers and the aromatic phosphate additives can be flame retardant to V-0 or 5V ratings at wall thicknesses of 2.5–3 mm or less. These blends are particularly useful for hospital applications where use of disinfectants and cleaners resulted in stress-cracking, whereas the presence of polysiloxane chains effectively improve the performance [156]. Recent GE patents show polycarbonates based on cyclohexylidenebis(2-methylphenol) blended with impact modifier, polycarbonate-polysiloxane copolymer and the usual bisphenol A bis(diphenyl phosphate) (BDP) as flame retardant, showing a balance of good flame retardant properties, good impact, flow and scratch resistance [157, 158].

Interestingly, the flame retardancy of polycarbonate-polymethylsiloxane block co-polymers depends more on the size of polysiloxane blocks than on the polysiloxane content [159, 160]. Small blocks of about 40 units tend to produce small bubbles in the char which makes it intumescent. The blends of PC and polymethylsiloxane at the same proportion form char with open voids instead of bubbles.

GE researchers [161] have found that blends of siloxane copolymers, notably siloxane polyimides, with polyaryl esters or polyaryl ester carbonates containing linkages derived from

resorcinol, bisphenol A, phosgene, terephthaloyl chloride and isophthaloyl chloride show improved flame resistance compared to conventional polycarbonates. Transparent flame retardant blends can be prepared. The compositions show good melt processability, high impact strength, high elongation, and as sheets and films they can have a peak heat release, as measured by FAR 25.853, of less than 65 kW/m^2 .

A polycarbonate resin composition, said by Idemitsu [162] to exhibit an excellent balance of fluidity, rigidity, heat resistance, impact resistance, recyclability and flame retardance uses dihydroxybiphenyl as part of the divalent phenol content.

7.8 Structural Approaches (Laminates)

A laminate approach by GE inventors [163] makes use of a first layer of polycarbonate, polycarbonate-polysiloxane copolymer, impact modifier and polyetherimide, where the polycarbonate is over half the weight of the composition; this layer is compounded to produce a low smoke density. The underlying layer allows more formulation latitude.

The carbonate can be part of a multilayer composite, where the covering layer is optically dense in the infrared, such as a metal. A Bayer disclosure [164] gives a specific example with a protective layer of SiO_2 , a 500 nm functional layer of copper, and a 100 nm coupling layer of chromium applied by electron beam vapor deposition on a polycarbonate. The composite showed a long ignition time and slow flame spread.

7.9 Modified End Groups

Polycarbonates with 90 % or greater fluoroalkylene carbonate end-groups are formed from a partially fluorinated alcohol or a partially fluorinated polymeric alcohol (introduced by means of the chloroformate) during polymerization, according to GE inventors [165]. These polycarbonates show high water contact angles, fluorine enrichment on the surface layer of molded articles, and good flame retardant properties and are useful in a variety of applications including medical (especially for blood contact), automotive, telecommunication and weatherable applications. With the addition of a sulfonate salt such as potassium perfluorobutanesulfonate, UL 94 V-0 or V-1 ratings can be obtained at 1.5 mm thickness.

7.10 Conclusions

A wide variety of brominated additives are effective in polycarbonates. A leading example is the tetrabromobisphenol A polycarbonate oligomers, but other aromatic bromine compounds can be used.

Polycarbonates have an unusual ability to be flame retarded with very low levels of alkali metal organosulfonates, such as potassium perfluorobutylsulfonate, potassium diphenylsulfone sulfonate and sodium trichlorobenzenesulfonate. These salts appear to have a catalytic mode of action. They can be used in combination with other types of flame retardants.

The ability of polycarbonate-ABS blends to be flame retarded with aryl phosphates has favored the usage of these blends in electrical and electronic enclosures. To avoid the vapor emission problems of triaryl (mono)phosphates during processing, di- and oligomeric phosphates have been successfully developed. The leading ones in the U.S. are resorcinol bis(diphenyl phosphate) and the more hydrolytically stable bisphenol A bis(diphenyl phosphate) generally sold as mixtures with higher oligomers.

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8 Commercial Flame Retardancy of Unsaturated Polyester, Vinyl Resins, Phenolics and their Composites

8.1 Introduction

This chapter covers three main classes of commercial flame retardant thermoset resins — the unsaturated polyesters, the vinyl esters (often made from epoxies), and the phenolics. Epoxies are covered in a separate chapter. Other thermoset types, such as triazines, cyanates, bismaleimides, furfural and urea-aldehyde resins tend to be inherently difficultly flammable and are thus outside of our scope. The main applications of all of these resins that we have included are in composites, which can replace metal, wood and concrete, with advantages in weight reduction, ease of fabrication and in many cases, lower cost and better corrosion resistance. The mechanical techniques used to make composites from these resins are outside the scope of this chapter.

The most commonly used unsaturated resin is unsaturated polyester due to ease of fabrication and relatively low cost. When ignited, unsaturated polyesters burn with substantial production of black smoke due to the presence (usually) of polymerized styrene units in the structure. The main applications where flame retardancy is required for unsaturated polyester resins are in ducts and other process equipment in chemical plants and paper mills, also in public transportation, aircraft parts, motor covers, belt guards, water-cooling towers, boats, and architectural parts. Most of these products are glass-reinforced composites. Because of the very large applications where flame retardancy is not required, such as underground pipe, mine bolts and many marine applications, the percentage of flame retardant resins relative to all unsaturated polyester resins is shown in one market research report to be less than 2 % [1]. The large use of alumina trihydrate (ATH), mainly for aesthetic and hardness properties other than flame retardancy, in artificial stone (synthetic marble, onyx) is probably not included in this number.

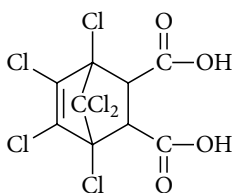
Frequently used tests in the US for these thermoset resins are the ASTM E-84 25-ft. tunnel (a rate of burn test called for in many building codes), the E 162 radiant panel, the E-662 NBS smoke chamber, and the ASTM E 1354 cone calorimeter rate-of-heat release test. Fire tests used in all parts of the world are discussed in a book by Troitzsch [2] and those most commonly used in the US are briefly discussed in a chapter in the present book.

8.2 Halogen-Containing Unsaturated Resins

A general review of unsaturated polyester resins is found in a book by Gum *et al.* [3].

The chlorine- and bromine-containing unsaturated polyester resins have a long history, going back to the 1950 era. An early review on flame retardant polyesters was published by

Stepniczka [4]. The original Hetron® resins were made at the Hooker Chemical Company in Niagara Falls and were based on “HET® Acid” (chlorendic acid, see structure below) made by addition of maleic anhydride to hexachlorocyclopentadiene (now made in Europe). These chlorendic acid-derived polyesters are still commercial, in Ashland’s group of Hetron corrosion resistant polyester resins [5]. Their flame retardancy has been overshadowed by their excellent chemical resistance. AOC has recently developed a highly corrosion resistant chlorendic polyester resin, usable even with nitric and hydrochloric acid at 55 °C, and meeting E-84 class I with 3 % antimony oxide [6].



At the present time, a limited range of flame retardant halogenated polyester resins are made using tetrabromophthalic anhydride. The flame spread for these halogenated resins is substantially less than for unhalogenated resins but the smoke is substantially higher for the halogenated resins [7]. Halogenated resins made from tetrabromophthalic anhydride, appear to be available only from Ashland at the present time. Antimony oxide is typically added to those resins as a synergist.

A relatively newer version have been introduced as AOC’s Firepel® K130, which can meet ASTM class I on flame spread and smoke without the need for fillers and with less than 35 % styrene. It is suited for uses as composite shields for motors, cooling towers and ducts where the higher corrosion resistance of a vinyl ester resin is not required [8].

The addition of decabromodiphenyl ether (“decabrom” or “deca”) is a common practice in flame retarding unsaturated polyester resins. An example of use of decabrom in a sisal (natural fibers) based composite has been discussed in a recent paper by Fonseca *et al.* [9] As with most other halogenated plastics, when strict flame retardancy requirements must be met, or the halogen level reduced for any reason, antimony oxides (commonly, antimony trioxide) are used as synergists. Flame retardant polyester resins depending on bromine, either as reactive or additive, are generally more costly and have higher specific gravity than non-halogen resins. Fabricators therefore need to purchase more pounds of resin to make a part of specific size. By the use of 1.5–3 % antimony trioxide or the translucency-favoring antimony trioxide/pentoxide dispersion, the necessary amount of halogen can be cut to about one-half. Moreover, by use of colloidal antimony pentoxide, less settling, better penetration of any reinforcement, and near-transparency can be achieved.

Antimony oxide can be replaced wholly or in part by zinc borate, often with some improvement in smoke, particularly with those resins containing aliphatic halogen, such as the chlorendates, or with vinyl resins based on tetrabromobisphenol A [10]. Although they are more expensive than zinc borate, it is reported that zinc stannate or zinc hydroxystannate (BA Chemicals, UK, Marshall Additive Technologies, US) can completely replace antimony trioxide in unsaturated polyester formulations [11, 12]. Apart from flame retardancy, zinc stannates

also show substantial reduction in smoke density [13]. With significantly higher prices of antimony trioxide, the use of zinc stannates becomes more commercially feasible.

Low styrene resins, probably tetrabromophthalic/isophthalic acid types, have been introduced by AOC. These are available either with more halogen and no antimony oxide or with about half the halogen content plus antimony oxide synergist [7].

Although aromatic chlorine is much inferior to aromatic bromine, tetrachlorophthalic anhydride is also used on a rather small scale to make specialty polyester resins. These chlorine-containing resins have lower smoke generation than their bromine analogs, and are currently available from Ashland for chemical resistance applications.

In past decades, serious efforts were made to find cheaper ways to introduce bromine into unsaturated polyester resins. Direct addition of elemental bromine to some of the double bonds of a polyester resin made from tetrahydrophthalic anhydride or a dicyclopentadiene-maleic anhydride adduct was done by Reichhold [14] as a low cost method for producing a flame retardant resin. Subsequently, this type of product was discontinued by Reichhold, apparently because of problems associated with the use of methylene chloride as solvent for the bromine addition, and perceived risks of elemental bromine. Reichhold does offer bromine-containing polyester resins such as their Dion® FR7704 and 7767.

Dibromoneopentyl glycol, formerly available from Dow, now available only from ICL-IP, Israel as FR-522 is useful to make flame retardant unsaturated polyester resins [15, 16] having relatively good light stability (the aliphatic C-Br bond is not cleaved as easily by light as the aromatic C-Br bond). This diol has an advantage in regard to affording good translucency in flame retardant polyester composites. Ashland's unsaturated polyester resin Hetron® FR 1440 is based on this diol. It is useful for container panels, for example.

8.3 Vinyl Ester Resins

The vinyl ester resins tend to be somewhat higher in cost than the unsaturated polyester resins but may be preferred where their better mechanical properties (toughness) and chemical resistance are important. The production volume is much smaller than that of unsaturated polyesters.

Tetrabromobisphenol A, made on a large scale and reasonably priced, is used in thermosetting resins in several ways. The largest use, in epoxies, has been reviewed by the present authors in a separate chapter. The bis(2-hydroxyethyl) ether of tetrabromobisphenol A behaves like a normal diol in polyesterification and can be used to make unsaturated polyester resins, although it has had little use. However, a more important use of tetrabromobisphenol A in unsaturated polyesters is to make vinyl ester resins. The diepoxides made from tetrabromobisphenol A, such as the diglycidyl ether, can be ring-opened with acrylic acid or methacrylic acid to give the so-called vinyl ester resins, or epoxy vinyl resins. These cure to thermosets in the manner of unsaturated polyester resins, generally with styrene added, and the resultant thermoset products are especially favorable for corrosion resistance in acidic and alkaline environments, and tend to have better impact and thermal shock resistance than most unsaturated polyesters. They are available from Ashland, Dow, and AOC. Significant applications are in the wastewater, power and chemical process industries where a high degree of flame

retardancy is required. Typical equipment using these resins is filament-wound, hand lay-up and spray-up tanks, pipes, ducts, stacks, scrubbers, linings or other equipment handling corrosive gases or liquids. As usual with halogenated resins, antimony oxide is added as a synergist. Ashland's Hetron® FR992Sb already has the antimony incorporated, with means for retarding settling.

Some of the vinyl ester resins can meet ASTM E-84 class I flame-spread rating, particularly with antimony oxide added. For example, Reichhold's Dion® 9300 can give < 25 flame spread if 1.5 % antimony oxide is added.

Newer versions of these vinyl ester resins are coming into use with lower percentages of styrene, below 40 %, driven by air pollution regulations. An example is AOC's Vipel® K022, which can achieve lower emissions during fabrication, flame spread of 20 and smoke rating of 450, with good corrosion resistance and strength. One interesting application is in theme parks for large entertainment structures.

A recent application of vinyl ester resins is in chimney liners in flue gas scrubber installations, where both corrosive vapors and high temperature thermal stress puts demands on the liner durability. In tests run without antimony oxide synergist, glass-reinforced laminates of brominated bisphenol A epoxy vinyl ester resin and a brominated epoxy novolac vinyl ester resin, commercially available from AOC, both survived thermal excursions up to 250 °C as well as long term aging at 177 °C without significant property degradation [17].

Another approach to building bromine into vinyl ester resins is to use dibromostyrene as part of the crosslinking monomer. This is shown in a patent, which may describe Glasteel's MC5 family of electrical laminate products with excellent high frequency/high voltage properties [18].

8.4 Hydrated Mineral Fillers

Alumina trihydrate as filler in unsaturated thermosetting resins has long been in use. The lower priced grades of ATH are used in artificial stone (solid surface, cast artificial marble or onyx, some of which is polyester, some acrylic) mainly for appearance reasons but flame retardancy is a "bonus". In sanitary ware, ATH of a higher grade is used at rather high loadings, providing good appearance, lower cost and flame retardancy. The flame retardant effect depends on a combination of the endothermic effect of dehydration of ATH, the fuel-diluting and flame velocity retarding effect of the released water, the replacement of combustible polymer by noncombustible mineral, and the build-up of a noncombustible barrier and enhancement of char. Comparison of ATH and silica [19] or Aswan clay [20] at the same loading level in unsaturated polyesters, showed obvious advantages of ATH, especially in smoke reduction. Further developments in this area include surface-treated grades of ATH which show improved corrosion resistance and even improved fire and smoke properties [21–24]. Finely precipitated and in some grades surface coated, ATH in Albemarle's Martinal® OL series, are said to have improved processing and improved thermal stability [25]. Improved flame retardant formulations have been demonstrated in polyester resins and vinyl ester resins by increasing the tolerated loading of ATH, while avoiding excessive viscosity, by using a specific size distribution (advantageously bimodal) and/or surface modification.

Some manufacturers of artificial stone use ground gypsum which is cheaper than ATH. It is a dihydrate and provides some flame retardancy by endothermic dehydration and dilution of fuel [26]. Gypsum can also be partly replaced by calcium carbonate which is still cheaper but is not very effective as a flame retardant, mostly acting as an inert additive.

8.4.1 Combination of ATH and Decabromodiphenyl Ether (“Decabrom” or “Deca”)

A cone calorimetry study at Huber [27] in a typical neopentyl glycol-isophthalic bulk molding compound (BMC) compared ATH or ATH plus calcium carbonate with decabromodiphenyl ether plus antimony oxide and combinations of ATH with decabrom plus antimony oxide. This study showed that decabrom plus antimony oxide gave benefits in regard to peak rate of heat release and effective heat of combustion but not in regard to time to peak rate or time to ignition, and adverse results in smoke and carbon monoxide, reflecting mainly vapor phase action. Addition of ATH to the decabrom-antimony oxide formulation gave linearly increasing benefits in all parameters except maximum smoke (D_m). ATH added alone gave equal or better benefits on all parameters except effective heat of combustion.

8.5 Low Smoke Polyester Resins

Smoke levels are reduced when ATH is used as flame retardant, but are still high by some standards because of the aromatic content (especially the styrene) in unsaturated polyester resins. When low smoke properties are required in a composite, the use of methyl methacrylate (MMA) in place of styrene is advantageous. It is more usual to replace only a part of the styrene by MMA. Flame retardancy can be achieved by using high loadings of ATH but ordinarily higher than 60 phr gives unhandleable viscosity. The increase of viscosity is usually in the range of 20–50 %. Although composites containing 60 phr ATH show low smoke and maintain most of physical properties, fatigue tests revealed much shorter lifetime of the composites [28]. A modification of the resin by Curry (AOC) allows 150 phr ATH to be used instead of the usual 60 phr, and these formulations, particularly a halogen-free version, are very low in smoke and low in toxic combustion products [7].

Low styrene unsaturated polyester resins can also be made using dicyclopentadiene as part of the crosslinking system. A representative one is AOC's Firepel® 133. Besides helping heat resistance, this monomer (probably because of increased crosslink density) is favorable to achieving flame retardance with lower flame retardant levels than comparable high styrene resins [29]. However, some examples of Firepel® 133 formulations show use of 150 phr ATH.

8.5.1 Low Smoke Unsaturated Acrylate Oligourethane Resins with Alumina Trihydrate

The relatively newer family of Modar® oligourethane unsaturated resins might be classified as polyesters but they are sufficiently different so that they are called modified acrylic resins. These were originally developed at ICI [30–32] and acquired by Ashland in 1993. The Modar®

resins, which have low viscosity and rapid cure, are crosslinked with methyl methacrylate or blends thereof with styrene, and they have unusually favorable smoke properties. They can be flame retarded with ATH (100–160 phr) to combine flame retardancy with low smoke, for demanding applications, such as electrical conduits, cable trays and switch boxes, architectural panels, fascia and trim (especially in theme parks), doors, ducting, interior marine decking, and paneling for public transport vehicles. They also are useful for making pultruded parts, many of which need to be flame retarded. A recent Spanish publication [33] shows many examples of optimization of halogenated as well as halogen-free low viscosity Modar® resin formulations based on Ashland's Modar® 835 S resin.

Using 160 phr ATH in Modar, it is possible to obtain Class I rating in the E-84 tunnel test and the NFPA Room Test. For reliable flame retardancy, it is advisable to carry out an adequate post-cure. If the composites are used for exterior sheathing, it is preferable that they should pass also the ASTM E-119 and ASTM E-136.

8.6 Phosphorus-Containing Flame Retardant Polyester Resins

The use of triethyl phosphate, tris(2-chloroethyl) phosphate, tris(2-chloroisopropyl) phosphate or dimethyl methylphosphonate as low viscosity liquid additives for ATH-filled resins for sanitary ware has been commercial practice for several decades. This approach permits the use of very high filler levels which would have been difficult to handle otherwise because of their high viscosity. Flame retardancy is obtained as a “bonus” [34, 35]. These rather volatile compounds seem to be well locked into the thermoset and do not cause water-sensitivity as evidenced by their use in polyesters for bathtubs and shower stalls.

In early study it was shown that triethyl phosphate and dimethyl methylphosphonate are beneficial at 0.2–0.7 wt. % P for reducing flame spread in halogenated unsaturated polyesters [36]. Interestingly, that higher use of these additives (*e.g.*, 1.0 wt. %) actually results in an increase in flame spread, perhaps by interfering with the cure.

One of the less desirable features of the use of the phosphates or phosphonates is that they tend to complex with cobalt-based cure promoters, and thereby slow down the cure. The problem can usually be overcome by increasing the catalyst. Another means is by heating, which for open mold applications may cause styrene emission problems. It can also be overcome by adding more peroxide catalyst. Another effective means is adding dimethylaniline to activate the peroxide, but this usually causes discoloration. Akzo Nobel has found some novel cobalt catalysts which have pre-complexed cobalt cations, which are less prone to complexation and deactivation by the phosphate or phosphonate [37].

Alternatives to ATH in electrical, construction and transportation use of unsaturated polyester resins are coated stabilized red phosphorus (RP) and ammonium polyphosphate (APP; high molecular weight water-insoluble type). These are often combined with lower levels of ATH. For example, in a glass reinforced polyester resin of a type used in electrical equipment, 15–25 parts of APP (Exolit® 422) or 10–15 parts of RP (Exolit® RP 654) and 50 parts of ATH give UL 94 V-0, whereas about 225 parts ATH alone would be required (a difficultly high loading for a glass reinforced resin). If maximum water resistance is required, a coated APP (Exolit® AP 462) should be used. Advantages of these lower ATH loadings are of course lower

viscosity and lower product density. Combinations of red phosphorus, ATH and a nitrogen additive such as melamine cyanurate are claimed to be advantageous regarding flame retardancy [38]. APP can also be used in flame retardant gelcoat formulations for railway vehicles [39]. It is claimed that combination of 150 phr of ATH with 50 phr of APP (or 225 phr of ATH + 25 phr of APP) can give an LOI up to 100 for pultrusion profiles [40]. Although ATH suppresses the intumescent performance of APP it is still believed that ATH and APP are synergistic in unsaturated ester composites [41]. An additive recently introduced by Lanxess, dimethyl propylphosphonate (Levagard® DMPP), was suggested for use with APP with a very small amount or no ATH [42].

Several years ago, Chemtura (Great Lakes Chemical at that time) introduced a char-forming solid organophosphate additive NH-1197 (CN-1197) for unsaturated polyester resins; it is a bicyclic structure made from pentaerythritol and a phosphorylating agent such as phosphorus oxychloride. This compound, relatively costly compared to simple triethyl phosphates, appears to have found use as a char-forming flame retardant additive where low smoke is a critical requirement [43].

8.6.1 Phosphorus Reactives in Unsaturated Polyester Resins

There is a substantial literature on reacted-in phosphorus components in unsaturated polyester resins [44–47] but almost all of these products were not commercialized. It might seem that phosphorus ester structures could be easily introduced into a polyester resin. However, what almost inevitably happens is that it is difficult to get complete esterification with a phosphorus acid; etherification side reactions take place, a high acid number tends to persist, and the moderately strong phosphorus acid causes further hydrolytic instability.

The use of unsaturated phosphorus monomers has not been successful to date, probably because of cost and poor copolymerization characteristics [48].

Polyester resin chemists have tried many approaches to circumvent these difficulties. Economics, reproducibility and resin quality problems have stood in the way of success. A recent US patent to researchers at the Industrial Technology Research Institute (Taiwan) shows transesterification of simple phosphorus compounds such as dimethyl methylphosphonate into unsaturated polyester resins [49]. Recently Clariant was granted a patent on use of 2-methyl-2,5-dioxo-1-oxa-2-phospholan (the KoSa® flame retardant for polyester fibers) in unsaturated polyesters [50].

For a time, an unsaturated vinylphosphonate (Stauffer's Fyrol® Bis-Beta) was used as part of the curing system for an unsaturated polyester resin which was briefly commercial [44]. Cost seems to have killed this product. Even though many phosphorus monomers have been described, unfortunately, there is no sufficiently inexpensive phosphorus monomer that can be used in place of part of the styrene.

8.6.2 Phosphorus-Melamine Combinations in Unsaturated Polyester Resins

Melamine itself, or combinations of melamine with ATH, have had some claims of utility as flame and smoke inhibitors in polyester resins [51]. Polish researchers showed that melamine

phosphate is useful to enhance flame retardancy in a chlorendic acid-based polyester resin [52, 53].

Industrially sponsored research at Polytechnic University [54] showed that inexpensive formulations made by high-shear dispersion of melamine in uncured polyester resin followed by high-shear addition of “superphosphoric acid” (fertilizer grade acid) afforded flame retardant results without halogen in low styrene resins. With high styrene resins, addition of triethyl phosphate or dimethyl methylphosphonate was needed to provide vapor phase action. These patent-free formulations, being low in cost, are believed to have commercial potential.

Recent development at Clariant showed high efficiency of aluminum phosphinate salts in combination with ATH, APP or melamine [55] or melamine polyphosphate [56]. For example combinations of 10 wt. % aluminum diethylphosphinate and 10 wt. % melamine polyphosphate provides V-0 rating in 30 % glass-filled composite and shows an OI of 42. Aluminum diethylphosphinate can also be pre-dispersed in polyester/styrene prepolymer.

8.7 Borates in Unsaturated Polyester Resins

Studies in Poland have shown that zinc borate, ammonium pentaborate and especially melamine borate are effective as partial or complete replacements for antimony oxide in halogenated polyesters [57]. The halogenated resin appears to have been epichlorohydrin-based. Some commercial usage is implied.

Recently, Clariant showed beneficial combinations of aluminum diethylphosphinate, (Exolit® OP 930) with zinc borate or zinc oxide [58, 59].

8.8 Phenolic Composites

Phenolics are amongst the oldest family of synthetic resins. A general review of this family of thermosets is available in a 1999 book by Gardziella *et al.* [60]. Gradual evolution has overcome some of the brittleness problems and has resulted in some outstanding present-day phenolic composites from a flame resistance standpoint and with quite acceptable physical properties to compete with composites based on unsaturated polyesters and vinyl ester resins. The dark color of phenolics can be covered by a paint or a gel coat. In-mold primers can also be applied to facilitate painting with low smoke-low toxicity paint systems.

Phenolic laminates, even without any flame retardant additive such as ATH, have difficult ignitability, very low flame spread, low heat release rates, low smoke and low toxic fumes. Typical values [61] for a painted phenolic with 35 % glass are: ASTM E-162 flame spread, 0.85 (cf. class 1 < 25), ASTM E 662 smoke density 0.6 in 1.5 minutes, Ds maximum 51, time to maximum 14 minutes, NBS smoke chamber gas analysis: 100 ppm CO, 80 ppm SO₂, zero HF, NO₂, HCl, HCN. ASTM E-84: flame spread 5 (compare class 1 < 25), smoke density 10. Autoignition temperature: 475 °C. Oxygen index > 55.

For extremely demanding fire- and smoke-avoidance situations such as theme parks, a comparison of various thermosets showed that by far the best performance under simulated

fire conditions was demonstrated for a phenolic glass laminate containing 30 % ATH [62]. This laminate uses proprietary resol chemistry (control of water release) to achieve high elongation, and thus overcome the brittleness which usually has been characteristic of phenolics. It is even tough enough to be used for a helicopter landing pad. By use of vacuum infusion, the composites can be made more quickly than with traditional prepreg methodology. In the E-84 tunnel test, a remarkable flame spread of 5 and smoke rating of zero can be achieved. Phenolic composites have been especially well accepted in Europe where there are stringent flame and smoke requirements, such as in the London Underground, passenger ships, other mass transit, offshore oil platforms and French theme parks [63]. The problem of mold corrosion caused by the acid curing catalyst can be avoided by use of composite vinyl ester molds, stainless steel or plated steel. It is quite important that the water release in curing is complete enough so that steam will not cause disruption of the thermoset under conditions of fire exposure.

Reinforced phenolic resins meeting very stringent flame, smoke and toxic gas requirements such as MIL-STD-2031, have been developed for applications such as submarine [64]. A patent application [65] indicates the use of ATH to improve flame retardancy and possibly silicone to improve flexibility and impact resistance.

8.9 The Effect of Glass Reinforcement on the Fire Performance of Reinforced Unsaturated Polymer Composites

Very detailed studies made using the cone calorimeter and another type of rate-of-heat-release device, which showed that for brominated polyester resins and resol phenolics, the average heat release rate was little affected by the glass level, although time to ignition increased and burning time decreased with increased glass [66, 67]. The phenolics had an advantage over the polyester in regard to flame spread.

8.10 Protective Veils

Fluorocarbon polymers such as ethylene chlorotrifluoroethylene copolymer (Halar®) can be used to protect pipe and ducts against corrosion and flame. An example would be Composites USA's Dual Guard® 2000. Low flame propagation and low smoke are found by UL 444 or by Factory Mutual's Clean Room Materials Test Protocol 4910. This material can be used both inside and outside of ducts. This approach to flame retardancy is of course not limited to polyester resins.

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9 Flame Retardants in Commercial Use or Advanced Development in Polyurethanes

9.1 Introduction

The main applications of polyurethanes are in rigid foams, flexible foams, coatings and elastomers. The closely related isocyanurate foams, which are often partly polyurethanes, are included in the present chapter. Flame retarding is dealt with only briefly in monographs on polyurethanes such as by Szycher [1] and Oertel [2]. A comprehensive review of flame retardants for polyurethanes was published in 1975 by Papa [3]. Another comprehensive and non-selective review covering the more recent literature and patents has recently been published by the present authors [4].

It should be mentioned that the term “combustion modifiers” is preferred rather than “flame retardants” by some in the industry to avoid giving the impression that such ingredients will prevent ignition and burning under all conditions. Moreover, it must be recognized that the standards are based on small scale testing, and in general the “flame retarded” materials are combustible in a large real fire, *i. e.*, they are never “fireproof” (indeed, a term which should be considered obsolete and misleading).

9.2 Commercial Flame Retardance of Rigid Foams

Because of the frequent use of rigid polyurethane foams as thermal insulation in buildings (boardstock and panels for roofing and sheathing) and transportation (refrigerated trucks and rail cars), there are many circumstances where flammability and smoke regulations must be met. A short description of some important tests is given in a chapter of this book, but a good summary of the many tests used throughout the world is available in the handbook by Troitzsch [5]. Typically, building code standards are applied; in the U.S. many of these are based on ASTM E-84, the 25-foot Steiner tunnel. Class A (class I) has a flame spread index of 0–25. Class B (class II) a flame spread index of 26–75, and class C a flame spread index of 76–260 (the flame spread indices are calculated from observed flame spread rate by a formula). A larger scale test, required for some insurance purposes, is the Factory Mutual corner test. Insulated roof decks, a very important market for rigid foams, are rated in the US by the Factory Mutual (FM 4450) roofing test [6], wherein fuel contribution rates in a specified calorimetric test must fall below a certain level to permit Class I to be achieved. Efforts have been made to find correlations between small scale tests and large scale tests, with some moderate successes [7–10].

Rigid foams, often made into sandwich structures, are used in many types of panels, shelves, equipment housings, doors, and other structural applications, sometimes requiring flame retardancy depending on the end-use. In sandwich or laminate structures, the surface to which the foam is laminated plays an important part in its fire resistance.

A recent (as of 2002) US-oriented discussion of fire code requirements in buildings is presented by Ross and Hagan [11]. A short overview and more recent update of regulatory standards and tests for the USA and Europe can be found in a paper by Landry [12].

9.2.1 Additives in Rigid Foams

The leading method for flame retarding rigid foam is to use additives, although reactive diols are occasionally employed where there is some special requirement. The leading additives are tris(2-chloroethyl) phosphate (TCEP) (ICL-IP Fyrol® CEF, Albemarle Antiblaze® 79, Lanxess Disflamoll® TCEP) and tris(1-chloro-2-propyl) phosphate (TCPP) (also known as tris(chloroisopropyl) phosphate) (ICL-IP Fyrol® PCF, Albemarle Antiblaze® 80, Lanxess Levagard® PP). Both of these are fairly low viscosity liquids, made from phosphorus oxychloride and ethylene oxide or propylene oxide. Their moderate volatility is not a problem in rigid closed-cell foams.

A typical formulation, using the pentane blowing agent, for a 1.8–2 lb/cu.ft. foam such as might be suitable for a roofing laminate is as shown in Table 9.1.

Table 9.1 Formulation for a 1.8–2 lb./cu.ft. Pentane-Blown Foam

B Component	Parts by wt.
Aromatic polyester polyol	100
Tris(chloroisopropyl) phosphate (Fyrol® PCF)	15
Silicone surfactant L6912	2.5
Water	0.5
Tertiary amine catalyst (C5)	0.32
Potassium octoate catalyst (T-45/K15)	2.68
Cyclopentane/isopentane blowing agent	23
A Component	
Polyisocyanate (PAPI 27) (NCO index 300)	196.7

This foam would be expected to attain Class I by the FM roofing test and Class II by the ASTM E-84 test. If E-84 Class I is needed with foam of this type, a brominated diol (discussed below) might be included.

One distinction between TCEP and TCPP as additives for rigid foams is that the chloroisopropyl phosphate, because of “steric hindrance,” is much more hydrolytically stable and unreactive toward the amine catalysts used in foam-making [13]. Nevertheless, TCEP is adequately stable in many formulations and has been used widely in polyurethanes. Where shelf-life of a premix is important, a substantial advantage will be found with TCPP over TCEP. The stability of a water-containing premix system is favored by use of the more hydrolytically stable flame retardants, avoiding strong amine catalysts and by use of hydrolysis-resistant aromatic polyols [14]. TCEP is particularly beneficial when it is used at 7–9 parts in combination with 6 parts of sucrose in isocyanurate foam for roofing application [15]. Because TCEP is receiving unfavorable risk assessment in Europe (suspected carcinogen, “Cat. 2” and show-

ing evidences of chronic toxicity, potential labeling “R45”) its production completely stopped in the EU and is significantly declining in other geographic areas.

A non-halogenated phosphorus additive, which has had usage in rigid polyurethane foam for a long time, is dimethyl methylphosphonate (DMMP). This compound contains 25 % phosphorus, the basis of its high flame retardant activity, and only about 8 phr is required in a sucrose-amine based rigid foam. This compound has “R46” (mutagen) labeling in Europe and therefore is not used much there. Diethyl ethylphosphonate or triethyl phosphate are also used for the same purpose, and have better label status in Europe. Lanxess has more recently introduced dimethyl propylphosphonate (Levagard® DMPP) which they advocate as a replacement for the halogen-containing flame retardants [16]. It is a low viscosity liquid, less volatile than the methylphosphonate [17].

Triethyl phosphate (TEP, available from many manufacturers) along with a specific polyester polyol was recommended in a R-245fa water co-blown polyurethane or polyisocyanurate roofing spray foam to meet fire standards [18, 19]. Increased use of triethyl phosphate was not dictated by halogen-free policies but associated with the need to decrease viscosity of the formulation and smoke (for further details, see below in the discussion of blowing agents).

Triaryl phosphates, specifically triphenyl phosphate, isopropylphenyl diphenyl phosphate, tricesyl phosphate and trixylenyl phosphate, all find some use in rigid foam formulations. A blend of triethyl phosphate and triphenyl phosphate, Lanxess Levagard® TPP, is used in rigid polyurethane and isocyanurate foams, particularly in Europe. It is sometimes combined with the reactive diol phosphonate (Lanxess Levagard® 4090N or ICL-IP Fyrol® 6 — see below).

Also, for non-halogen applications of importance in Europe, high molecular weight finely-divided ammonium polyphosphate (APP, Clariant Exolit® AP 422 or Budenheim Iberica's FR CROS® 484) has been found effective in pentane-blown polyurethane or polyisocyanurate foams. These demand enhanced flame retardant additive levels to overcome the adverse flammability effect of the pentane. The use of APP, which works by a solid phase mechanism, also provides lower smoke compared to halogen-containing foams of similar density according to Clariant workers [20]. Dispersions in polyol are available. Ammonium polyphosphate (APP) is also useful in rigid integral skin foams.

Ammonium polyphosphate formulated with a char former and blowing agent to make a complete intumescent system is also useful in both rigid and some flexible foams. These formulations containing Exolit® AP 750 can meet many requirements of railway and aircraft standards for integral skin rigid and flexible polyester foams. For example, rigid foam panels containing APP, pentaerythritol and some powdered aluminum can withstand a Bunsen burner test at 1200 °C due to formation of a thermally stable protective char [21]. The high viscosity of the ammonium polyphosphate dispersions makes them somewhat difficult to use.

Stabilized red phosphorus also has some usage in Europe in rigid polyurethane foams. It is highly efficient on a weight basis, and can be used at rather low loadings to meet stringent flammability standards. For example, 7.6 %wt. red phosphorus, 7 %wt. TEP and 3.2 % APP allow to pass DIN 374 and GB 822 test in rigid PU foams [22]. Dispersions of red phosphorus

in polyol, castor oil or tris(chloroisopropyl) phosphate are variously available from Clariant or Italmatch.

Fillers such as expanded clay, expanded glass, slate, or the like may be added for various reasons. Limited data suggests that layered clays like montmorillonite, particularly after quaternary ammonium treatment to favor exfoliation, will reduce the rate of heat release. The addition of long glass fiber reinforcement to foam board is likely to provide improved fire resistance [23].

Aluminum hydroxide (ATH) is a flame retardant filler which is finding its way in rigid PU foams, especially in the view of development of halogen-free formulations for a B2 rating in the DIN 4102-1 test [24]. Formulation composed of ATH, APP and Rhodia's cyclic phosphonate Amgard® (former Antiblaze) NR-25 was designed for passing the more severe E-84 tunnel test with a class 1 rating without the use of halogenated fire retardant [25].

Graphite flakes intercalated with sulfuric acid and carefully washed in order to neutralize excess sulfuric acid and to seal graphite galleries on the edge of the flakes is known as a good flame retardant for non-acid-sensitive polymers. Upon fast heating by the flame, sulfuric acid boils in the galleries and also oxidizes graphite. The evolved gases disintegrate the graphite layers and greatly expand them, to fifty times or more the original volume [26]. More recently, expandable graphite finds its application in rigid PU foams and many formulations based on expandable graphite have been developed [27–29]. The expansion ratio of the graphite significantly diminishes with decrease of the particle size of the graphite. Dispersing of relatively large particles is a challenging engineering problem, and special mixing machines have been developed by Canon [30]. Expandable graphite is particularly efficient in rigid PU foams in terms of smoke reduction, but it is less efficient in isocyanurate foams [31]. An obvious disadvantage of expandable graphite comes with worsening of thermal insulation properties of the foam, which can be slightly improved by addition of TEP [32]. The color, electrical conductivity and granularity of expandable graphite also retard some possible uses.

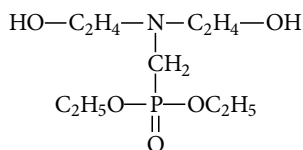
9.2.2 Reactive Flame Retardants – General Comments

Over several decades, much effort has been put into developing diols or polyols containing phosphorus and/or halogen, as a means for building flame retardancy into the polyurethane structure by chemical bonding [3]. There is often a belief that this approach will lead to greater permanence, although experimental evidence for that benefit is hard to find. On the other hand, practice has shown some disadvantages of using reactive flame retardants versus additives. For example, it becomes difficult making reproducible flexible PU foam with the right density and the right cell openness if the hydroxyl number (mg KOH/g) of the reactive flame retardant is much higher than that of the polyol. Rigid PU foams are less sensitive to hydroxyl number, because rigid polyols in general have much higher OH number than flexible polyols, and reactives have found a place in rigid foams. Although reactive phosphorus- or halogen-containing flame retardants are on the market, it is believed that the use of additives is dominant in both rigid and flexible polyurethanes.

9.2.3 Reactive Flame Retardants in Rigid Polyurethane Foams

An early reactive diol, Vircol® 82, was marketed for some years by Albright & Wilson, and more recently by Albemarle (Antiblaze® PR82). It is the reaction product of dibutyl acid pyrophosphate with propylene oxide and is a substantially neutral diol with about 11.3 % P and an OH number of about 205. Its main application has been in rigid polyurethane foam prepolymers and premixes, where it facilitates the compatibility of the ingredients as well as providing its flame retardant effect.

A reaction product of diethyl phosphite with formaldehyde and diethanolamine was invented in the 1960s at Victor Chemical Works and has the structure (see below). This product is now sold by ICL-IP (as Fyrol® 6) and Lanxess (as Levagard® 4090N). The primary hydroxyl groups readily react into a urethane structure. It has primarily been used in spray foams or pour-in-place foams, and reportedly in urethane elastomers. Because of the reacted-in aspect, it has sometimes been chosen for applications where the foam will be subjected to severe long term heating, as for example in a stadium dome; other uses are in large refrigerators. Good retention of the flame retardant can be assured [33]. The amino group in the molecule has some catalytic contribution to the foaming (a practical advantage in spray foams), and also may have some buffering (stabilizing) effect on the finished foam. Since the phosphorus ester group is not in the backbone of the polymer, if it suffers hydrolysis, it does not represent cleavage of the polyurethane structure. Formulations of Fyrol® 6 in polyol have good shelf life. The mode of action of Fyrol® 6 may be increased char yield [34].



9.2.4 Impact of Blowing Agent on Flame Retardancy of Rigid Foams

The chlorofluorocarbon blowing agents have been phased out in January 2004 as a second stage of phasing out fluorinated blowing agents (after CFC) to avoid their upper-atmosphere ozone-depleting action [35]. The use of pentane (cyclopentane, isopentane, n-pentane or mixture) for the blowing of foams in place of chlorofluorocarbon blowing, imposes needs for a higher degree of flame retardancy, to counteract the flammability of the blowing agent. The usual flame retardants such as Fyrol® CEF and Fyrol® PCF can still be used but the level will usually have to be raised. Atlas Roofing has developed a formulation blown by cyclopentane, acetone and water, where 15 parts of Fyrol CEF is predicted on the basis of a small scale test will provide a pass for FM 4450 [36]. The higher the isocyanurate index, the less the required flame retardant level to meet a standard. Because of potential fire hazard, pentane blowing agent can be used only for boardstock or other limited in-plant production where specially engineered fire-safe ventilation is available [37].

Also in response to this major technological shift in blowing agents, some new flame retardants have been introduced as alternatives. For example, Clariant has introduced the

oligomeric phosphonate diol, Exolit® OP 560, discussed later. It has about 12 % P content and OH number of 400, and it is recommended where emissions from flexible foam must be minimized [38, 39].

Other new non-ozone-depleting blowing agents containing halogen can allow for less flame retardant, or with a high enough isocyanurate content, no flame retardant at all. After many years of development 1,1,1,3,3-pentafluoropropane, available as Honeywells’ Enovate® 3000 (HFC-245fa) or Solvay’s HFC-365mfc, has become the product of choice in spite of relatively high price. This compound does have a flash point, but can be made less flammable by blending with tetrafluoroethane [40]. There is also a possible trade-off in the use of a pentane with HFC-245fa. The pentane lowers the cost of the blowing agent but may require an increase in the flame retardant. Honeywell data from Williams [41] (Table 9.2) shows some comparable boardstock formulations, the last three said to have similar costs. The flame retardant TCPPP has been elevated to compensate for the pentane. Mixtures with pentanes are much more economical than the use of HFC-245fa alone.

Table 9.2 Flame Retardant Boardstock Formulations Using Isopentane and HFC-245f, (ENOVATE® 3000)

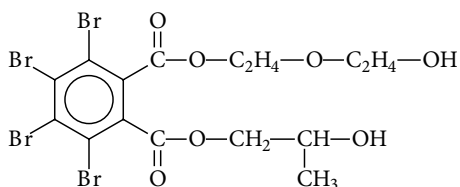
Quantities and properties	Enovate 3000	Isopentane	Isopentane and 2 % Enovate 3000	Isopentane and 10 % Enovate 3000
Index	250	300	300	300
FR (TCPP), php	0	10.00	9.00	7.50
Water, php	1.00	1.00	1.00	1.00
Enovate 3000, php	40.00	0	1.00	4.50
Isopentane, pbw	0	20.90	20.40	18.75
Density, lb./cu.ft.	1.70	1.90	1.90	1.90
k-Factor, relative	0.90	1.00	0.97	0.95

In spray foams HFC-245fa is usually combined with water in the ratio of 4:1 in order to decrease vapor pressure of HFC-245fa in storage tanks and optimize blowing performance. Pentane cannot be blended with HFC-245fa in spray foams for fire safety reasons. Because of high water presence in spray foams, more urea groups are made at the expense of urethane groups and the foam becomes more flammable and generates more smoke. An increased portion of polyester polyol at the expense of Mannich polyol and blending of Fyrol® PCF with TEP helps decrease smoke and pass the E-84 tunnel test (class II). The blend of HFC-245fa with water does not help cut the viscosity as effectively as the old chlorofluorohydrocarbon system (141b) did. This is another reason for using TEP along with Fyrol® PCF in spray foams, especially in cold weather.

Other examples of halogenated blowing agents that can lower flame retardant requirements are 1,1-dichloroethane and trans-1,2-dichloroethylene. These chlorohydrocarbons are suggested for use in combination with pentane [42, 43].

9.2.5 Brominated Alcohols as Reactive Flame Retardants

Some brominated diols are also used in rigid urethane foams. Chemtura (former Great Lakes) PHT-4 Diol® (similar to Albemarle Saytex® RB-79) made from tetrabromophthalic anhydride (see chemical structure below) has been available for many years and is used mainly in rigid foams to meet ASTM E-84 Class I or II ratings. This product has one primary hydroxyl group (faster reacting) and one secondary hydroxyl group (slower reacting). It is a viscous liquid with about 46 % bromine content. A related tetrabromophthalate diol with both hydroxyl groups primary, thus more reactive, has been introduced by Chemtura as Firemaster® 520. Albemarle also introduced new brominated polyols Saytex® RB 9130 and 9170 which are said have low viscosity [37]. Based on patent literature these could be products of oligomerization of Saytex® RB 79 with aliphatic diacids [44].



With 25 % Saytex® RB-79 in the polyol and 25 parts of TCPP (Fyrol® PCF) per hundred parts of polyol at an index of 300, a borderline E-84 class I could be reached. According to more recent Albemarle data, with a 350 index, 25 % RB-79 and 25 parts PCF, a firm class I was reached, with smoke density about 100.

With selected polyols, low smoke can also be achieved even with bromine in the polymer, according to information from Great Lakes Chemical (Chemtura) [45]. It has also been recommended in a blend with a liquid phosphate (Albemarle Saytex® 7980) for pentane-blown isocyanurate roofing foams. A blend of RB-79 with tris(chloroisopropyl) phosphate was said to perform particularly favorably in this application [46].

Tribromoneopentyl alcohol $(\text{CH}_2\text{Br})_3\text{CCH}_2\text{OH}$ dissolved in tris(chloroalkyl) phosphate is the basis for the SaFRon® 6600 line of products from ICL-IP [47, 48]. The SaFRon 6600 products are very efficient and because of this they are used at relatively low addition levels. In Europe these products are recommended for reaching German class B2 according to DIN 4102, part 1 as well as for reaching the French M1 class according to NF P 92-501. SaFRon® 6700 allows reaching a very high level of fire retardancy in rigid foams with medium isocyanate indices.

Chlorine and bromine-containing polyols (Solvay's Ixol® family) have been in use for some years, particularly in Europe. This family of polyols is believed to comprise the reaction products of epichlorohydrin with 2,3-dibromo-2-butene-1,4-diol [49]. They are effective for permanent flame retardancy of rigid polyurethane and polyisocyanurate foams [50, 51].

9.2.6 Non-Halogenated Polyols Favorable to Flame Retardancy in Rigid Foams

Some early studies at Uniroyal showed that amine-initiated polyols favorably affect flame retardancy [52].

Polyols containing aromatic rings, such as the “Mannich polyols” made from diethanolamine, formaldehyde and phenols, are favorable to flame retardancy not only because of the nitrogen content, which also provides some foaming catalysis, but because the phenolic rings enhance char formation during burning [53]. Rigid water-blown foams with much-improved flame retardancy can be made using combinations of an ultra-low viscosity Mannich polyol with another polyol, according to Dow [54].

The use of aromatic terephthalate polyester polyols (functionality 2.0–2.3) of the Invista Terate® family can contribute not only some improved compressive strength and thermal stability but can also substantially enhance flame retardancy such that the phosphorus or halogen flame retardants can be greatly reduced, according to Invista product information. This flame retardant benefit is because of the char-formation propensity of the aromatic backbone structure. Terate® polyols are inexpensive and are based on byproducts or coproducts of terephthalate manufacture. They are typically used at levels up to about one-third of the polyol for 2–2.5 lb./cu.ft. density foam, the limiting factor being the high equivalent weight of the Terate®. Higher density foams can use even larger amounts of a Terate®. They are also useful in isocyanurate foams. Terate® polyols of the 2.1–2.3 functionality are most useful in bunstock, panel, pour-in-place, spray and foundry systems. Terate® polyols of 2.0 functionality show improved processability in laminates as well as the other systems. The optimum Terate® choice also is affected by the blowing agent used.

In order to improve physical properties and flame retardant performance for foams blown with R-245fa, Oxid developed a new highly aromatic Terol® 708 polyol [19] with high functionality. Terol® 708 has higher functionality than the previous generation highest functionality Terol® 256. Cone calorimeter prediction indicates that Class I E-84 pour-in-place foams can be made with this polyol.

An improved polyol was developed at DuPont by co-reacting an aromatic polyester polyol with sorbitol [55]. It is said that, using this polyol, only about 4 parts of TCPP is needed to pass ASTM E-84 and FM 4450 tests with a class II rating.

Polyols made from natural renewable sources are a new trend in flexible PU foams, but to a certain extent they are also used in rigid and isocyanurate foams. It was found that a soy-oil-based polyol is better in terms of thermal stability and flame retardancy than a polypropylene oxide polyol in rigid PU foams [56]. It is unlikely that it will be comparable with aromatic polyols, however it may have an advantage of low smoke evolution.

9.2.7 Additives in Isocyanurate Foams

The isocyanurate structure is much more thermally stable than a urethane structure (which can undergo the reverse reaction of its formation, back to isocyanate and alcohol). Thus, a substantial degree of inherent flame retardancy can be built into a rigid foam by using an excess of isocyanate relative to co-reactant hydroxyl groups and catalyzing the isocyanate to trimerize to the very stable isocyanurate ring. A totally isocyanurate foam can be made,

but in practice, most of these foams are partly urethane, partly isocyanurate. The higher the isocyanurate content, the greater the char yield on fire exposure and thus the more flame resistant, but also the more brittle (friable). Moreover, the isocyanate is more costly than the polyol. An additive phosphate, usually TCEP or TCPP, is often added, mainly to reduce friability, but flame retardancy is also enhanced. Isocyanurate foams with no added flame retardant can be used to make, for example, composite panels, and if properly covered, will pass most building code standards.

For demanding applications in roofing, a detailed study shows good fire performance in the revised large scale tests from pentane-blown polyisocyanurate foams containing TCEP, or a mixture of dimethyl methylphosphonate (DMMP) and RB-79 (tetrabromophthalic ester diol), or alternatively, Saytex® XP-4020 [7].

It was shown by experimental work at Albemarle that a flame spread index of 23 (class I) and a smoke density of 100 (E-84 tunnel) could be attained by using an isocyanate index of 350 with 25 % Saytex® RB-79 and 25 parts of TCPP, according to Albemarle.

9.2.8 The Effect of Catalyst Choice on Flame Retardancy of Rigid Lamination Foams

Trimer modification (isocyanurate formation) of rigid polyurethane foams has been gaining importance because this method not only allows the use of lower cost polyester polyols (like Terate) but also allows significant lowering of the level of the additive flame retardant. Pentane blowing agents can also be used as a partial alternative to water blowing, allowing a somewhat lower index and thus saving on the cost of the relatively more expensive isocyanate. The catalyst used to produce the foam controls the amount of trimer, and thus affects the flame retardancy at a given level of flame retardant, since trimer structure is favorable for flame retardancy. In a careful multi-variable study of a wide range of catalysts, using diethyl ethylphosphonate as the additive flame retardant, potassium octoate was found advantageous over potassium acetate as a trimerization catalyst in regard to foam flammability as measured by flame height (German DIN 4102 test B2). Strong blowing catalysts such as pentamethyldiethylenetriamine also appeared slightly better than strong gelling catalysts in regard to flame height. The use of a special pentane emulsifier allowed for less, or even zero, water in blowing the foam [57]. With more pentane, more flame retardant additive or higher isocyanurate content would presumably be used to compensate for the unfavorable flammability effect of the pentane.

9.3 Flame Retardance of Flexible Foams

The three largest markets are transportation, furniture and carpet backing. Carpet backing uses mostly alumina trihydrate as the flame retardant additive, the other markets use an ever-increasing variety of approaches. More recently there was significant activity in the United States in an attempt to introduce a Federal standard for upholstered furniture. The original proposed tests, involved the fabric, the filling and the total assemblage [58]. However, at the end of 2007, CPSC under the pressure of upholstered furniture industry manufacturers

issued new proposals including only a smoldering test of the upholstery fabric and excluding PU foam testing. A detailed discussion is outside the scope of this chapter, and would be subject to change as regulations evolve. A recent (2008) update of fire tests and regulatory status in the USA and Europe can be found in a paper by Landry [12].

9.3.1 Additives in Flexible Foams

A major fraction of the flexible polyurethane foams used in furniture is flame retarded. Additives are the dominant means, although much research has been expended on reactives. In general, the flame retardant additives increase the foam ignition temperature and reduce the rate of flame spread [2].

To pass the Federal automotive standard MVSS 302, typical additive levels for seating foam are about 16 parts per hundred of a chloroalkyl phosphate in 1.0 lb./cu.ft. foam, and about 7 phr in 1.8 lb./cu.ft. foam. For simple horizontal testing of ½" thick seating foam, even lower levels may pass MVSS 302. On the other hand, when the foam is laminated to a fabric (often untreated and with less than ½" foam), and the test is run with the fabric facing the flame, it is more challenging to pass the MVSS 302.

Furniture manufacturers in the U.S. usually try to have their foam cushions comply with the CAL (California) 117 tests. This is usually done with liquid plasticizer-like additives, containing phosphorus or halogen or both. Typically, about 16 parts per hundred of a chloroalkyl phosphate is sufficient for 1.0 lb./cu.ft. foam and 12 parts for 1.8 lb./cu.ft. foam, and in some cases even lower levels suffice. The addition of a small amount of melamine can prevent failure to pass the test after repeated flexing. In the UK, and perhaps eventually throughout the EU, a stringent fire safety standard must be passed by seating cushions. Thus, for UK use, to pass BS 5852, flame retardant levels are generally higher and melamine is generally used at more substantial levels. Melamine is often used in combination with these additive flame retardants, and is discussed below at greater length.

Both tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCP) are used extensively as additives for flexible polyurethane foams. Of these, the most frequently used is TDCP (ICL-IP Fyrol® FR-2, Albemarle Antiblaze® 195), a product of reacting epichlorohydrin with phosphorus oxychloride. Ring opening of the epoxy group gives mostly the branched structure (the 1,3-dichloro-2-propyl group), with a few percent of the straight chain (the 2,3-dichloropropyl group). Some older literature references mistakenly call this product tris(2,3-dichloro-1-propyl) phosphate, mostly before the true structure was established. Actually, the fact is that the product is mostly branched but a small straight chain content keeps it from crystallizing, except on long storage under cold conditions. TDCP tends not to interfere with catalysis and allows considerable latitude in the tin component. It allows early development of resistance to compression set.

A typical present-day formulation in slabstock or automotive seating foam is shown in Table 9.3 (in parts by weight). The MVSS 302 results are given as distance burned and time to extinguishment in accordance with the test protocol.

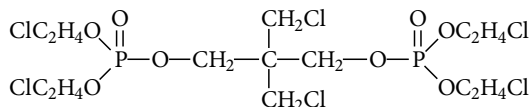
Cold-cure molded foam can meet the standards with lower levels of TDCP. Hot-cure molded flexible foam tends to need a somewhat higher percentage of flame retardant. Here, TDCP is

Table 9.3 Formulation for A Flame Retardant Slabstock or Automotive Seating Foam

Component; flame test	Parts by wt.
Polyol, 3000 Mol. Wt.	100
Silicone L-5750	1.20
Water	3.85
Amine, Dabco® 33-LV	0.30
Tertiary amine, NIAx A-1	0.20
Stannous octoate 50 %	0.42
Methylene chloride	1.50
80:20 TDI (Intex III)	51.2
Fyrol® FR-2	12.0
Flammability by MVSS-302	1.4" distance 0 s extinction

9.3.2 Additives in Flexible Foams – Volatility Considerations (“Fogging”)

When slightly volatile additives such as TDCP are used as flame retardants in automobile seating foams, there is often a detectable fogging of the inside of the windshield if the passenger compartment of the vehicle is warm [59]. Other components of the foam, such as the catalysts and surfactants can also contribute to the fogging. There are various industry tests for windshield fogging [60]. Where the monophosphate fails this test, it is usual to use diphosphates or oligomeric phosphates or phosphonates.



9.3.3 Halogen-Free Additives for Flexible Foams

An oligomeric ethyl phosphate additive containing 19 % phosphorus has been marketed by ICL-IP as Fyrol® PNx. Because of the high % phosphorus, it is quite efficient and as little as 4–8 php is effective in passing the California 117 test and MVSS 302 in a 1.5–1.8 lb/cu.ft. foam [61, 62]. Because of the low addition level, this additive has the advantage of low fogging propensity for automotive applications.

Triaryl phosphates, such as isopropylphenyl diphenyl phosphate, find some use in flexible foam formulations sometimes in combination with a bromine-containing additive (see Scorch discussion). A more recent introduction, Chemtura's Rheofos® NHP, a low viscosity liquid, probably a member of the aryl phosphate family [63], is a formulation designed to meet MVSS 302 for hot-molded automotive seating, said to be cost effective and non-fogging. Lanxess's Disflammol® DPK, also a member of the triaryl phosphate family, is recommended for both furniture and automotive low fogging application [64].

In polyester-polyol-based flexible foams, which have a greater charring propensity than polyether-polyol-based foams, the insoluble high molecular weight ammonium polyphosphate, crystal type II, is especially useful as a low-smoke non-migrating flame retardant additive. It is available as a finely divided powder (several suppliers) or as a thixotropic dispersion (Clariant Exolit® AP 452). To minimize interactions with other foam components, a more expensive resin-coated variety may be used such as Exolit® AP 462.

9.3.4 Overcoming the “Scorch” Problem in Flexible Foams

In the manufacture of water blown flexible polyurethane foams, allowing the foam to reach an excessively high temperature during the latter stages of foaming, can lead to “scorch.” This is, minimally, a discoloration of the interior of the foam slab or bun, more seriously a loss of mechanical properties indicative of structural degradation, and in extreme cases, a fire can result. Scorch is aggravated by excessively fast foaming, by warm ambient conditions as might occur on a hot summer day, by drafts, by a formulation imbalance or metering malfunctions, by traces of soluble iron or copper compounds [65], and by the presence of some not very thermally stable flame retardants. Aminophenyl oxidation products are blamed for most of the discoloration [66].

Those flame retardants which are either most reactive towards the hypothesized arylamino groups, or simply less thermally stable, tend to be those which aggravate scorch. Therefore, as a class, the aliphatic phosphates tend to be more prone to aggravating scorch than the aromatic phosphates. The less thermally stable, the more aggravating. Chloroethyl phosphates are scorchie than tris(1-chloro-2-propyl) phosphate [67]. Tris(1,3-dichloro-2-propyl) phosphate is still less scorchy but still requires avoidance of excessively high exotherm temperature. Deep insight into the chemistry of scorch was given by a study done at University of Turin [68, 69] sponsored by Akzo Nobel. They found spectroscopic evidences of presence of aminophenylamido structures in the foam, which are known to be readily oxidized to quinoneimine structures which are extremely chromophoric with very strong visible light absorption bands. The formation of the chromophoric groups is aggravated, amongst other factors, by the presence of flame retardants with alkylating capabilities such as the

chloroalkyl [70] or alkyl phosphates, chloroparaffins or brominated aliphatic hydrocarbons, and this alkylation reaction also adds to the exotherm; moreover, the alkylated aminophenyl structures are more easily oxidized to quinoneimines. Conversely, phosphorus or bromine compounds that cannot alkylate amino groups are those which do not aggravate scorch; examples are aryl phosphates or aromatic brominated compounds.

Scorch can be lessened by various antioxidant “packages” [71–75]. The common antioxidants of the 2,6-di-*tert*-butylphenol type, which are often used in the polyols, are not too effective by themselves as scorch inhibitors, and may themselves generate yellowish quinoidal chromophores. ICL-IP offers a low scorch version of TDCP under the trade name Fyrol® 38 containing an antioxidant package. A highly effective antioxidant for preventing scorch was Ciba’s aromatic lactone HP-136 [76] or packages based on this powerful antioxidant [73]. Subsequently, HP-136 was removed from the market, but new lactone type stabilizers may replace it [77].

The polybromoaromatic compounds have unreactive bromine atoms and act as inert additives under the conditions of scorch, thus foams containing them tend to be scorch resistant. Consequently, a widely used low scorch flame retardant additive has been a liquid blend of pentabromodiphenyl ether and isopropylphenyl diphenyl phosphate/triphenyl phosphate, both quite stable liquids [78] which perform well together. Either component alone is effective only in very undemanding applications such as MVSS 302 seating, although pentabromodiphenyl ether had viscosity problems. In the early 2000 era, environmental concerns regarding pentabromodiphenyl ether [79] has led to a sharp decline in its usage, and regulatory actions in Europe have the effect of a ban. Manufacturing of pentabromodiphenyl ether was voluntarily suspended in the USA and the foamers have also been seeking alternatives.

Alternatives introduced into the market include a tetrabromobenzoate ester, Great Lakes (Chemtura) Firemaster® BZ-54 [80, 81] which can be used alone or blended with an alkylphenyl diphenyl phosphate. When used alone, this 54 % bromine content additive has a favorable effect on flame lamination, and also unlike the pentabromodiphenyl oxide formulations, it does not cause center softening in high resilience foam formulations. Its blend with an isopropylphenyl phosphate may be Chemtura’s Firemaster® 550 and 552, used in both high-resilience and conventional foams [82–84]. The more recently introduced Firemaster® 600 is said to be 10–20 % more effective than Firemaster® 550, and is likely to contain tris(butoxyethyl) phosphate [85].

Because of steric hindrance and absence of a hydrogen on the carbon atom adjacent to the bromine-bearing carbon, the bromoneopentyl alcohols are quite stable to hydrolysis and to dehydrobromination. This reactive product is offered by ICL-IP as FR-513. FR-513 is soluble in polyols, chloroalkyl phosphate esters and aromatic phosphate esters. Because of the presence of a free primary hydroxyl group, it reacts with the isocyanate during foaming and becomes an integral part of the polyurethane network which makes it resistant to extraction [86]. Blends based on FR-513 and stabilized with antioxidant packages to reduce scorch are marketed by ICL-IP as SaFRon® 7700 [48].

ICL-IP is also offering low-scorch additive type flame retardants based on phosphate esters. Fyrol® HF-4 is a halogen-free flame retardant with good hydrolytic and thermal stability and it is designed for furniture and automotive foams where low scorch is a primary consideration

[87]. Fyrol® FR-7 contains phosphorus and halogen. Because of this, it is more efficient than Fyrol® HF-4, but slightly less scorch resistant.

Albemarle entered the low scorch flame retardant PU market with the phosphorus-bromine flame retardant Saytex® RX 8500 where the bromine part is reactive with PU foam. Based on the patent literature this product is most likely a combination of brominated diol Saytex RB-79 and isobutylated triaryl phosphate stabilized with an antioxidant package [88]. It contains 28 wt. % bromine and 2 wt. % phosphorus and is recommended for flexible slab stock and molded PU foams. Saytex® RZ 243 is another phosphorus-halogen flame retardant from Albemarle which is said to be scorch resistant. Another Albemarle additive Antiblaze® RX-35 apparently combines chloroalkyl phosphate and bromine flame retardant technologies and is also said to be scorch resistant.

9.3.5 Reactive Flame Retardants for Flexible Foams

The diols used in rigid foams, such as Fyrol® 6, have too high an OH number for use in flexible foams, except in small amounts. A large amount of research has been done on reactive phosphorus-containing diols and polyols for flexible foams without much commercial success [3]. The reasons for the lack of success are mostly cost, adverse properties related to excessive hydrophilicity, and the need for more reformulation to accommodate reactive flame retardants in each foam grade for each application.

A newer halogen-free phosphorus-containing diol was developed by Hoechst for rigid or flexible foams and it has been marketed as Exolit® OP 550 by Clariant [20]. The product is a hydroxyethyl terminated ethyl phosphate oligomer diol [89] with about 17 % P for rigid or flexible foams, especially for molded and high density slabstock flexible foams. It causes less plasticization than small molecular weight additives such as triethyl phosphate. The extent of market penetration of this product is unclear.

A related phosphorus ester reactive, Exolit® OP 560, with about 12 % P content and a higher OH number (400), is available where emissions from flexible foam must be minimized [90, 91]. It is mostly used in automotive flexible PU foams where it reacts in and becomes part of the PU network.

Clariant also has a related diol, Exolit® OP 514, with some chlorine content as well as phosphorus. Typical loadings of Exolit® OP 514 or 560 are 2–10 php to pass MVSS 302 and 6–12 php to pass CAL 117. A related OH-functional methylphosphonate methyl phosphate oligomer is available in the USA and China (formerly Supresta's Fyrol® 51 or Fyroltex® HP) but used mainly in paper and textile applications. It is not available in Europe at the present time.

In order to meet low fogging requirements Lanxess is marketing a monofunctional reactive all-phosphorus flame retardant Levagard® TP LXS 51053 [92]. Based on the recent patent literature, it could be dimethyl 2-hydroxyethylphosphonate [93].

9.3.6 Polyols Favorable to Flame Retardancy in Flexible Foams

Many cold-cured flexible molded foams can pass lenient flammability requirements, such as MVSS 302, with no flame retardant or very little. The combustion-modified high-resilience

(CMHR) foams are substantially more flame retardant with a given amount of flame retardant additive, and indeed some high resilience (HR) foams can pass some of the more lenient flammability requirements with no flame retardant added, probably because of their melt-flow characteristics. This mode of retardancy can be defeated by laminating or even being adjacent to a fabric which can retard the melt flow. CMHR or HR foams with a degree of inherent flame resistance were made by Mobay from grafted high molecular weight polyols with polyacrylonitrile grafts [94, 95] and/or dispersed styrene-acrylonitrile polymer [96], or from polyols with added polyurea dispersion (Bayer's PHD® polyols) [97]. In these systems, the more the surface melt is coherent and protective, the more flame retardant. To pass the stringent British Standard 5852, Part 2, Source 5, 20–30 parts by weight of melamine is usually added, usually along with a chloroalkyl phosphate.

It should in general be noted that foams with retardancy relying on melt-flow can be rendered flammable with even a small amount of an infusible solid, such as alumina trihydrate (ATH). Dow has introduced particular Specflex® polyols for use with particular MDI-type isocyanates which can provide improved flammability by the CAL TB 117 criteria in water-blown flexible foams over the entire isocyanate index range without the need for additive flame retardants [98]. The technology is based on high molecular weight base polyols in combination with co-polymer polyols, and all-MDI prepolymers with optimized isomer/oligomer ratio and hydroxyl-terminated components

A family of "PIPA" (Poly Isocyanate Poly Addition) foams require lower amounts of fire retardants to pass tests such as BS 5852 (Source 5). The choice of polyol seems to influence the melting properties. Although the softness of the foam can be controlled by the ethylene oxide content of the polyol, the softness seems to have little correlation to the fire test performance [99].

Polyols developed by Arco were found to yield slabstock foams which require little or no melamine to pass the Cal TB 133 or BS 5852 (Source 5) [100]. Avoidance of melamine avoids viscosity and cell uniformity problems.

Polyols with polymers dispersed in them so as to cause a lower temperature of decomposition were developed by Asahi Glass to favor passing the automotive standard MVSS 302 with no added flame retardant. The mode of action seems to be based on the endothermicity of the decomposition and also on the formation by the decomposed polymer of a viscous molten surface layer which shields the foam [101]. These polyols are said to function in hot molded, slab and low density HR foams.

9.3.7 Melamine in Flexible Foams

Especially in Europe, melamine is frequently used as part of the flame retardant system in flexible foams. Melamine, dispersed in selected polyols, is effective as a flame retardant additive in flexible foams for upholstered furniture or bedding, and affords acceptable comfort, foam strength and cost properties [102, 103]. In general, melamine does not affect the foaming process, but average cell size depends on the melamine particle size; the coarser the particles, the bigger are the average cells [104]. Melamine is used also in the US, but patents have imposed limitations on its use with some dispersed polymer-modified polyols [105–108].

The patented formulations allow for reduced levels of melamine, resulting in more stable dispersions and less impairment of the physical properties of the foam by the solid additive. Certain combinations of melamine with specific amine-based polyol-isocyanate condensation products provide enhanced flame retardancy [109]. The choice of specific BASF polyols, alternative to the CMHR types, with melamine has provided the basis for a successful series of flame-retardant furniture foams, some even passing stringent FAA aircraft seating requirements [110].

Melamine is often used in combination with a haloalkyl phosphate, such as tris(1-chloro-2-propyl) phosphate (TCPP). A representative CMHR (combustion modified high resilience) formulation to pass the British Standard 5852 (Source 5) is shown in Table 9.4.

Table 9.4 Representative CMHR Formulation to Pass British Standard 5852, Source 5

Component	Parts by wt.
PHD polyol, OH No. 33	100
Toluene diisocyanate (80:20)	46.2–57.7
Water	3.0–4.5
Melamine	20–30
Silicone surfactant	0.3–0.4
Triethylenediamine catalyst	0.15
Alkanolamine	1.5–2.0
Tin catalyst	0.13–0.15
Haloalkyl phosphate	2.0–10.0
Index	~105

A synergistic interaction has been noted with melamine and TDCPP (but not with the more volatile TCPP) in CMHR foam, and explained on the basis of a chemical interaction producing char or a difficultly ignitable low-melting semi-solid [111]. However, in commercial practice, this relationship is not seen and TCPP appears to be preferred.

Melamine can cause problems of viscosity increase, settling, plugging of the equipment, and non-uniform cell size problems. Attention to the grade of melamine (use of uniform fine particle size) can minimize the problems. Small particles such as DSM's type 003, with average particle size of 50 microns, may be preferred and have been shown to have a physical properties advantage; the best properties at a given melamine loading are said to be obtained if the melamine particles are smaller than the strut thickness of the foam [112].

The California standard 133 governing furniture in public places requires that the entire piece of furniture pass an open flame test. This more stringent requirement can be met if the foams also contain melamine, as well as a chloroalkyl phosphate flame retardant. In some formulations, ATH is also added but it should be noted that in some other formulations the addition of a solid such as ATH works against the flame retardant melt flow action. Combustion-modified high-resiliency foam used in high risk places such as hotels, hospitals and prisons may need a combination of several flame retardants to meet very stringent flame retardancy requirements.

9.3.8 Other Solid Additives in Flexible Foam

Where polyester polyols are used in slabstock instead of polyether polyols, some problems with hydrolytic stability are sometimes encountered. In Europe, finely divided ammonium polyphosphate is sometimes used as a flame retardant in polyester polyol based foams. It can be metered as a paste predispersed in polyol [2]. Such applications are mostly for applications where UL-HFI flame requirements for automotive under-the-hood applications must be met. Hydrated alumina (ATH) can also be used in flexible slabstock foams as an additive [2]. High loadings are needed, thus ATH tends to have problems of density, serious effects on mechanical properties, and settling prior to and during the foaming process.

9.3.9 Silicone Surfactants Favorable to Flame Retardancy in Flexible Foams

Polyether polysiloxanes are effective as foaming stabilizers and are commonly (although not universally) used for this purpose. The surfactants have a complex action on flammability by virtue of their effect in controlling cell opening and cell size [113, 114]. Besides their effects during foaming, the surfactants can affect melt rheology under flame exposure conditions. Silicone surfactants, if not optimum for this application, can actually increase flammability, or in other words, may require that more flame retardant be added to obtain a desired level of flame retardancy. One of the ways a surfactant can affect flammability is by its effect on cell opening and air flow, a complex and concentration-dependent effect [115]. A substantial minimizing of the requisite level of flame retardant in a flexible foam is made possible by the use of a silicone surfactant of a type designed for this application, such as Union Carbide's (later, OSI's) L-5740 and L-5750. Favorable factors appear to be the presence of a sufficient number of relatively low molecular weight polar (polyoxyalkylene) grafts and the optimum total ratio of these grafts on the dimethylsiloxane backbone [116]. OSI silicone products subsequently were acquired by GE Silicones and then by Momentive).

While there are now "universal silicones" such as OSI's L620, which are effective in both flame-retardant and non-flame-retardant foams, some manufacturers make available silicone surfactants which have been optimized for specific foam applications. For example, in the Byk Chemie Silbyk® family of silicone surfactants, recommendations are made for grade 9110 for flexible polyester slabstock, 9700 for CMHR slabstock, TP 3796 for rigid laminated boards and slabstock, TP 3706 or 3801 for laminated boards and metal faced sandwiches, and newly developed TP 3846 for flexible ether slabstock. The higher the surfactant activity, the lower the required surfactant loading which is generally better for flame retardancy.

Foamers who have to make foams passing the horizontal burn classification UL 94 HFI often prefer to avoid silicone surfactants. Two explanations bear upon the question of the deleterious effect on flammability seen with less optimum silicones: one is that degradation products of the silicone reduce melt viscosity, make more drips of smaller diameter, with more surface to have air access and to burn [Buescher, J. (Byk Chemie), private communication]. Another explanation, rather different, is that the silicone burns to silica which acts as a wick, stabilizing the flame; this effect can be demonstrated by applying powdered silica (or almost any other infusible powder) to a test specimen of flexible foam flame-retarded with a chloroalkyl phosphate [Weil, E. D., unpublished observations].

From a basic study, it appears that silicones can also improve flame retardancy by forming a siliceous barrier layer when burnt [117, 118]. This beneficial effect is most evident in reduction of peak heat release rate in the cone calorimeter.

Technology utilizing CO₂ as auxiliary blowing agent in flexible slabstock foam was introduced around 1993. Where flame retardant performance is required, some re-optimized silicone surfactants are preferred, for example OSI's NIAx® L-631, to obtain desired cell structure and adequate flame retardancy without requiring an excessive amount of flame retardant additive. Air Products DABCO® DC5980 is a relatively new high efficiency non-hydrolyzable silicone glycol copolymer which is also flame-retardant-compatible.

Recently, Momentive Performance Materials (ex. GE Performance Products) filed a patent on new silicone surfactant with specific ratio of acetoxy-capped polyether groups without branches, being > 75 % of total ethylene oxide content [119]. Apparently, this silicone is helping to produce fine cell structure which is beneficial for flame retardancy. Air Products has patented a family of polydimethylsiloxanes with a narrow distribution of oligomers, 90 % in the range of $n = 5-7$, which apparently is also beneficial for flame retardancy of PU foams [120].

9.3.10 Effect of Foaming Catalysts on Air Flow, Flame Retardancy and Smoldering Combustion

While it is desirable to have a good air flow (typically 3 cfm) in a conventional flexible foam in the 1.5–1.8 lb./cu.ft. range, it is detrimental to the flame retardant property to have a very high air flow (such as > 5 cfm) but some minimum air flow is necessary to allow proper cooling. Smoldering is also enhanced. Air flow is in fact one of the main properties of a foam affecting its fire behavior. Open cell vs. closed cell content is obviously related to air flow and thus to flammability. Foams with high air flow are desirable for good furniture cushioning. Moreover, the air flow will tend to increase with repeated flexing. Excessive initial air flow can generally be remedied by using a somewhat higher level of the tin catalyst, and this can be expected to improve flame retardancy and reduce smoldering tendency. Foams near the minimum acceptable air flow tend to be erratic in flammability. Experimental foams with poor cell opening (high closed cell content, very low air flow) can be deceptively flame retardant. Foams with high but desirable air flow may require additional flame retardant such as supplemental amounts of melamine to pass the ignition test requirement.

9.3.11 Interaction of Upholstery Fabric on the Flammability of Flexible Foam in Furniture

This is a complex topic beyond the scope of this chapter, but briefly discussed in our textile chapter. The fact that there is a strong interaction is in general well known, but specific combinations are unpredictable. An excellent summary was presented in 1998 to the Consumer Products Safety Commission to assist them in regulation and test development [121]. It was pointed out that bad combinations of fabric and foam can still occur as surprises, and in some instances even an interliner can cause a problem. Interliners, which are often used to meet mattress flammability standards, are discussed further in our textile chapter.

9.3.12 Effect of Fillers on Flame Retardancy of Flexible Foams

The use of non-flame retardant fillers such as calcium carbonate or barium sulfate may make a flexible foam more difficult to flame retard, unless very large loadings are present. Any infusible solid powder or fiber can provide a wick-like action and enhance burning. As mentioned, this effect can sometimes be seen in the deleterious effect of non-optimized silicone surfactants. Infusible pigments can sometimes have an adverse flammability effect, particularly on smoldering, so it is important to check flame retardancy if pigmentation is added or changed. Pigments containing iron, magnesium or calcium are reputed to be particularly suspect.

9.3.13 Rebonded Foam

This type of foam can use up to about 75 % scrap foam, and is useful for applications such as carpet underlay. Flame retardancy can be usually met by about 10 % of Fyrol® FR-2, which can assist as a fluxing aid in melt bonding.

9.3.14 Combinations of Polyurethane and other Foaming Polymers

Particularly low density polyurethane-polychloroprene foams made using Chestnut Ridge's reduced-pressure foaming process show a favorable combination of fire resistance and physical properties, such they are useful for aircraft seating, mattresses and other fire-regulated applications [122].

9.3.15 Basic Studies on Flammability and Flame Retardant Action in Flexible Foams

Foam density and type of foam were found to influence the ignition and burn rate — generally burn rate increases as density decreases — but there is also found a complicated interplay between char forming and melting [123]. A recent study at NIST showed that addition of nanoparticles to the foam helps to keep its integrity and prevent melting and dripping away [124]. However, nanoparticles do not help in passing CAL 117 test or even make it more difficult to pass.

In a study at Polytechnic University, the mode of action of tris(1,3-dichloro-2-propyl) phosphate (TDCP) in a flexible polyurethane foam was examined. Two modes of action could be discerned. In upward burning, as in the California 117 test, the main process seemed to be physical vapor phase action, since the TDCP mostly volatilized from fire-exposed foam undecomposed, produced no char, and acted as a retardant whether it was uniformly distributed in the foam or merely applied on the outside. When injected into the flame, it did not seem to act as an inhibitor, surprisingly in view of the prevalent idea of halogen compounds as radical-scavenging flame inhibitors. The foam itself also appeared to release toluene diisocyanate, particularly in the non-flaming preignition stage, leaving essentially difficultly-ignitable polyol behind. However, in downward burning, TDCP did help form a semi-charred "skin" so there was evidence of a condensed phase chemical action [125, 126].

9.4 Polyurethane Elastomers and Cast Resins

A wide variety of flame retardants are used here. In general, it appears that flame retardants are more effective in non-foamed elastomers; probably, this is because of less air access and lower surface/volume ratio in the elastomer. This relationship was shown by a cone calorimetric study comparing the effects of a variety of commercial flame retardants in foam and non-foamed urethanes [127]. One surprising result in this study was the efficacy of zinc stearate in lengthening time to ignition.

Insoluble high molecular weight ammonium polyphosphate, crystal type II, is useful in elastomers and cast urethane resins. It is effective at low levels of addition and affords generally low smoke. It is available as a finely divided powder (multiple sources) or as a thixotropic dispersion (Clariant Exolit® AP 452).

In Europe especially, there has been some use of red phosphorus as an additive for elastomers including polyurethane types, and polyol masterbatches or dispersions are available (from Italmatch or Clariant) which avoid the handling of the flammable red phosphorus powder.

ATH can be used in quite high loadings as a sole flame retardant or in combination with phosphorus additives, in polyurethane elastomers. ATH not only retards flame but also suppresses smoke. Mineral fillers such as ATH but also clays and mica also provide dimensional stability and reduction of thermal expansion, but with ATH alone, processing can be difficult because of viscosity. The level of ATH needed to reach a flammability rating of V-0 can be reduced by using ammonium polyphosphate, red phosphorus or a liquid organic phosphonate such as Rhodia's Amgard® (formerly Antiblaze®) 1045. For example, Clariant shows that V-0 can be reached by about 140 phr ATH and about 10 phr Exolit® 422 (APP) or Exolit® RP 652 (red phosphorus), where 350 phr of ATH alone would be needed in a particular cast polyurethane. Another phosphorus-based product which is synergistic with ATH is resorcinol bis(diphenyl phosphate) (ICL-IP's Fyrolflex® RDP) [128]. Apart from flame retardancy it provides plasticization and improves melt flow. Flame retarded cast polyurethanes can have good electrical properties, suitable for insulator applications, but care must be taken to select a particularly moisture-resistant (preferably coated) grade of ammonium polyphosphate or red phosphorus.

Melamine alone, at rather high loadings, is effective to pass moderate flame resistance requirements in polyurethane elastomers [129]. Both tris(1-chloro-2-propyl) phosphate and tris(1,3-dichloro-2-propyl) phosphate are effective in polyurethane elastomers. Where the halogen is undesired, it has been found possible to use tris(butoxyethyl) phosphate (ICL-IP's Phosflex® T-BEP). Diphenyl octyl phosphate (ICL-IP's Phosflex® 362) and other diphenyl alkyl phosphates can be used in polyurethane and other elastomers to obtain flame retardancy with relatively low smoke. Resorcinol bis(diphenyl phosphate) (Fyrolflex® RDP) is also very effective in combination with melamine. Melamine cyanurate may have some advantages over melamine [130] in combination with RDP.

Expandable graphite is useful as a flame retardant in polyurethane elastomers as well as in flexible foams [131] and has long been used in some European mattress and pillow foams (Dunlop). It is made from natural graphite by intercalating an oxidizing acid between the carbon layers. On heating, it typically expands mostly in the range of 235–300 °C [132].

This additive is used in gaskets and seals. It loses its effectiveness if finely divided, so some granularity must be tolerated.

9.5 Reaction-Injection-Molded Products

This technique is used to make various items such as machine enclosures and furniture parts. The same flame retardant additives useful for rigid foams can be used here.

An effective non-halogen reactive system, with good heat distortion properties and thus suitable for reaction injection molding, can be achieved by “fine-tuning” the OH number of a phosphorus polyol mixture comprising the high OH number diethyl N,N-bis(2-hydroxyethyl)aminomethyl phosphonate (ICL-IP Fyrol® 6 or Lanxess’ Baytherm®) admixed with the low OH number oligomeric phosphate phosphonate [133].

9.6 Urethane Coatings and Sealants

Polyurethanes are one of the several binder types used in intumescent coatings, which are outside the scope of this book. The typical formulation is a combination of a charring catalyst, (usually insoluble high molecular weight ammonium polyphosphate), a char-former (usually mono-, di- or tripentaerythritol) and a blowing agent (melamine can perform this function in coatings). Typically these three ingredients are in about a 3:1:1 ratio [134]. Polyurethane sealants, such as caulks and elastomeric strips, can be similarly formulated.

Non-intumescent flame retardant polyurethane coatings may be made using the brominated diols such as the diester diol from tetrabromophthalic anhydride (Albemarle’s Saytex® RB-79 or Chemtura’s PHT-4 Diol). As usual, antimony oxide may be added to boost the flame retardancy.

Firestops, which are flexible heat-expandable solids for plugging openings and gaps where pipes, conduits and cables penetrate through fire-rated walls, may be made from urethanes similarly formulated with intumescent ingredients. In some cases, hydrated alkali silicates or expandable graphite can be used as the intumescent agent. Ammonium polyphosphate and combinations thereof with intumescent char forming agents are often used. Other soft polymers are used besides polyurethanes. Polyolefins, various rubbers, plasticized PVC and silicones are found in this field of application. A detailed discussion is beyond the scope of this chapter.

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10 Current Flame Retardant Systems for Epoxy Resins

10.1 Introduction

This chapter covers materials currently available or which appear to be in serious development. The application areas for epoxy resins are electrical laminates and encapsulation resins, construction materials, adhesives and protective coatings. When cured, epoxies have good electrical properties, good adhesion, low shrinkage, and resistance to heat, to mechanical shock, to solvents and to chemicals. In each of the applications, flame retardancy is of importance, but particularly the electrical and coatings areas which we emphasize in our review.

10.2 Electrical and Electronic Applications

A general review of the many uses of epoxy resins in electronics is available in a book by Goosey [1]. Besides printed wiring boards (PWB) which is the largest application, epoxy resins are used elsewhere in electronics, in conductive adhesives, flip chip encapsulation, bonding of leads, die coatings, surface mounting adhesives, encapsulation and conformal coatings. The largest single flame retardant, costwise, is tetrabromobisphenol A (TBBA) used predominantly in printed wiring boards.

The NEMA classes of copper clad laminate PWBs are as shown in Table 10.1 (not a complete list). The FR-4 grade is a particularly important one and will be discussed at the greatest length. Usually, FR-4 boards will be formulated to pass UL 94 V-0. FR-5 is rarely used. High temperature applications often specify FR-4 based on IPC 4101/26 (T_g of 170–220 °C). Many consumer electric applications use CEM-1 boards that are flame retardant, as required by UL.

For higher temperature performance above that of FR-4, other resins notably polyimides, cyanates, PTFE, other fluoropolymers, epoxy-PPE blends, and even ceramics are often used. Special high frequency requirements such as computer circuits operating in the Gigahertz range also may require particularly low dielectric constant materials, such as PTFE or primarily hydrocarbon type resins. Mineral fillers such as silica are often present, which is favorable to flame retardancy. Polyimides, cyanates, PTFE and inorganic substrates are usually inherently flame retardant. Certain low dielectric constant crosslinked hydrocarbon-rich resins pose a more challenging flame retardancy problem.

The phenolic/paper boards have long been flame retarded with triaryl phosphates or oligomeric organic phosphates. In general, phenolic resins tend to help flame retardancy because of their char forming ability; on the other hand, the char may show glowing non-flame combustion (smoldering, “punking”) and phosphorus flame retardants help deter that problem. Aryl phosphates and oligomeric phosphates are also good plasticizers and help to improve flexibility of phenolic resin boards.

Table 10.1 NEMA Classes of Copper Clad Laminate Printed Wiring Boards

NEMA Grade	Resin, rein- forcement	Description	Typical uses
XXP, XXXPC	Phenolic, paper	Hot or cool punching	Inexpensive consumer items like calculators
FR-1 and FR-2	Phenolic, paper	Flame retardant XXP/XXXPC	Where flame retardancy is required
FR-3	Epoxy resin, paper	Flame retardant	High insulation resistance
CEM-1, -3	Epoxy, glass cloth, paper or glass core	Punchable epoxy, properties between XXXPC and FR-4	Radios, smoke alarms, lower cost than FR-4
G-10	Epoxy, paper, glass	Excellent electricals, water-resistant, not f.r.	Computers, telecom, cost above FR-2
FR-4	Epoxy, glass cloth	Like G10 but flame retardant, $T_g \sim 130^\circ\text{C}$	Where flame retardancy is required
FR-5	Epoxy, glass cloth	Like FR-4, more heat resistant, higher T_g than FR-4	Military, aerospace, where specified
FR-6	Polyester resin, glass mat	Flame resistant	Low capacitance, or high impact applications.

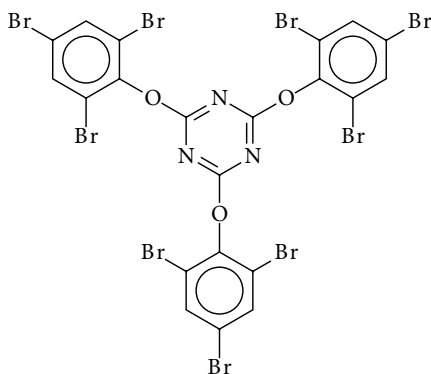
Encapsulated integrated circuits share many of the same considerations, but matching thermal coefficient of expansion is particularly critical. Therefore, high levels of fillers, as high as 80 % silica, are often used, as well as many of the same flame retardants used in PWB. A special test, UL 1694, suitable for small items is available, using a needle flame. This is a test of the encapsulated package itself rather than just of the plastic material [2].

10.3 Brominated Flame Retardants in PWB

As already mentioned, tetrabromobisphenol A (TBBA) is the single largest flame retardant in terms of commercial value at the present time. It is used in an estimated 95 % of all FR-4 epoxy printed wiring boards. Tetrabromobisphenol A is manufactured by several producers (*e.g.*; ICL-IP FR-1524, Chemtura’s BA-59P and Chinese producers) and is priced as a commodity. The means of incorporating it into the epoxy resin is by “chain extension”. This means reacting it in with a molar excess of diglycidyl ether of bisphenol A or other related epoxy, such that the resultant reaction product is still a di- or polyfunctional epoxide. This reaction must be accomplished without gelation. Special chain extension catalysts are used: triphenylphosphine, or ethyltriphenylphosphonium salts are amongst those reportedly used. The amount of tetrabromobisphenol A is usually such that the finished resin will contain about 18–21 % bromine.

As an alternative method of incorporating bromine into PWB, a preformed diglycidyl ether of tetrabromobisphenol A may be used. This is available as Dow DER® 542. It is suitable for use where maximum level of bromine is needed to offset a large ratio of hardener or non-brominated resin. Using DER 542, higher T_g values can be achieved at a given level of flame retardancy than with similar formulations using tetrabromobisphenol A as a chain extender. This bromine-containing diepoxide can also be used to offset large ratios of hardener or other non-brominated resin content, or in products where its higher cost is offset by improved properties [3]. Higher molecular weight epoxy resins made from tetrabromobisphenol A are also available from ICL-IP (F-2001 and F-2200) and Resolution (their EPON® Resin 5112 and 5114). These may be used as reactives in epoxy products or as additives in thermoplastics. The EPONs contain about 51 % bromine; for flame retarding cured epoxy resins, about 10–20 % Br is usually sufficient.

High frequency low dielectric loss PWB were developed at General Electric by replacing about 30–50 % of epoxy resin with polyphenylene ether (PPE). This system is currently marketed by Isola as GETEK®. Because of good electrical properties and better than TBBA compatibility 1,3,5-tris(2,4,6-tribromophenoxy)triazine (ICL-IP FR-245) (see structure below) is used at about 25 wt. % level in a GETEK formulation [4]. FR-245 additive also found use in recently developed LG Chem (Korea) PPE/cyanate ester/epoxy formulation [5].



10.3.1 A Challenge to Tetrabromobisphenol A

Environmental activists, especially in Europe and Japan, tend to oppose the commercial use of halogen compounds, such as bromine-containing flame retardants. TBBA has not escaped hostile attention. Some halogen compounds such as pentabromodiphenyl oxide (ether) amassed enough data to indicate that they become diffused through the environment and can be detected in aquatic animals, birds and mothers' milk. Pentabromodiphenyl ether has small but measurable vapor pressure and water solubility, and subtle toxicological effects [6]. Although the association is scientifically dubious, these adverse features tend to be ascribed by environmental activists to bromine compounds as a broad class.

The German Environmental Department (UBA) has issued a position paper in which they recommend phasing out TBBA and claim, along with various toxicological concerns, that it has been detected “in the food chain” [7]. In a rebuttal assessment of the report by BSEF (a bromine industry group), it is pointed out that the German paper fails to address the fact that in epoxy PWB, the compound is locked into the plastic by covalent bonding. It has been used, particularly in the Far East, as an additive flame retardant in inexpensive dark-colored styrenic plastic formulations, which may account for the cases where it has been observed as an environmental contaminant. Even so, the low toxicity even of the free tetrabromobisphenol A makes it a doubtful problem. It has low acute toxicity [8], no demonstrable hormonal effects, no neurotoxicity [9] does not bioaccumulate, and is rapidly excreted by mammals. A recent review on human exposure to brominated flame retardants revealed that TBBA was detected in river sediments in Japan and Sweden but it was not detected in human foodstuffs [10].

A documented assessment of the usefulness, toxicological and environmental issues regarding tetrabromobisphenol A in printed circuit boards and assemblies was prepared by the IPC (Association of Connecting Electronics Industries) [11]. Risk assessment of TBBA has been completed in Europe without significant risk findings [12]. In the free form TBBA is classified as “dangerous for aquatic organisms” and will carry label of R50/53 which will be effectively managed by proper product stewardship [13].

Another aspect which puts some pressure on the use of tetrabromobisphenol A in PWB is the recycling requirement of the EC [14]. Under the Waste from Electrical and Electronic Equipment (WEEE) regulation passed in 2002, the halogen-containing (also usually lead-containing) circuitry of a disposed computer, printer or other electronic device, would have to be separated and disposed of in a special waste site, at the manufacturer's responsibility. The cost of doing this is enough to cause some electronic companies (Motorola, for example) to avoid halogen. The impact of this directive on the use of TBBPA is not clear at the time of writing. An offsetting factor is that component separation from electronic equipment is also practiced for the purpose of metal recovery. There is also developmental technology for recovery of bromine from scrap [15].

The WEEE regulation was presumably stimulated by a highly publicized concern regarding formation of halogenated dibenzodioxins and dibenzofurans traces of which might be generated upon incineration of electronic waste containing halogens [16]. Detailed study of thermal decomposition of TBBA shows very low tendency of formation of dibenzodioxins and dibenzofurans from this compound [17]. In fact, studies of the incineration of PWB containing reacted-in TBBA show no enhanced halogenated dioxin formation under proper incineration conditions. Incineration with energy recovery has been shown to be practicable and safe, and a major outlet for electrical and electronic scrap in Europe is metal smelters [18]. This approach was demonstrated in a full scale trial in a Belgian metal smelter [19]. In Japan, where incinerators tend to be operated at lower temperatures, there has been more concern about halogenated dioxin formation. It has been shown that high temperature or the presence of calcium oxide during pyrolysis of bromine-containing circuit boards largely prevent bromodibenzodioxin or bromodibenzofuran formulation [20].

At the time of this review, this halogen-free vs. halogen issue is far from settled and there are many crosscurrents [21]. An industry assessment in 2003 [11] argues that the replacement of the halogen-containing circuit boards is unwarranted because there is no data on

illness or death associated with their use, and injuries and/or death are associated with non-flame-retarded electronic equipment. On the other hand, “green” pressures from environmental activist groups (who emphasize fear of halogenated dioxins) impinging on OEM marketers are having a real effect on creating demand, as reviewed by Clariant authors in 2006 [22]. The balance seems to hinge on cost and reliability. The long experience with the TBBPA epoxy systems is favorable for reliability.

It has been recently shown that many lives were lost to fires from electronic equipment, in particular TV sets, which were no longer being flame retarded by some European manufacturers [23]. Although the main issue here is the cabinet, not the PWB, the publication of this safety data has stimulated the return of European manufacturers to use of additives such as decabromodiphenyl ether, and would tend to support continued use of brominated flame retardants. Recycling the bromine and heavy metal content of electronic waste is also under serious development and may obviate the need for bans on bromine and lead.

One interesting case where an environmental label, the German “Blue Angel”, was awarded to a computer printer which was halogen-free except for the PWB. The labeling group mentioned that practical alternatives did not exist at that time for avoiding bromine in the PWB.

10.4 Non-Halogen Alternatives to Tetrabromobisphenol A

Companies wishing to exhibit a “green” image in the marketplace, particularly in Europe and the Far East, have announced halogen-free products. Recently a book has been published on various aspects of manufacturing “green” electronic products [24]. Various problems which remain for non-halogen FR-4 PWB are lower T_g , metal-resin adhesion, fabricating properties (especially drillability), dimensional stability, electrical properties (such as dielectric constant), long term reliability of electrical properties, and increased cost. It is interestingly to note that glass-mat and copper are responsible for about 75 % of the cost of FR-4 laminates [15]. Therefore, it is obvious that not only higher cost of flame retardant, but also difficulties in manufacturing of halogen-free laminates and low volume make them significantly more expensive than traditional TBBA based laminates. A review on reliability and manufacturing issues of “green” encapsulants was recently published by Lin *et al.* [25].

10.4.1 High Loadings of Metal Hydroxide Fillers

For FR-4 PWB, it has been challenging to achieve the V-0 rating without excessive loading of endothermic mineral fillers, such as ATH, without sacrifice of thermal stability and moisture resistance, and without a substantial cost increase. Some improvement particularly in thermal stability can be made by use of curing through crosslinking reagents having hydroxyl groups instead of using dicyandiamide [26, 27].

It is difficult with ATH alone to reach a sufficient level for a FR-4 rating, since at 60 parts per hundred of resin (phr) copper adhesion is reduced. It is possible to reach UL-94 V-0 levels in 1.6 mm thick CEM-3 (epoxy with woven glass surface and non-woven glass core) using 200–250 phr thermally stable aluminum hydroxide ($\text{Al}_2\text{O}_3 \cdot 2.7\text{--}2.8\text{H}_2\text{O}$, Martinal® TS-610 or

TS-601 from Albemarle. Even better results are predictably obtainable with some phosphorus chemically incorporated into the epoxy resin [28, 29]. Special grades of ATH with improved thermal stability achieved by special crystallization and aminoalkylsilane treatment [30] or through additional purification and decreasing sodium content [31] were recently developed at Albemarle.

Especially in Japan, high loadings of ATH and (sometimes) $\text{Mg}(\text{OH})_2$ have been used. There are processing problems in performing the laminating process, due to high viscosity and aggregation of the filler. Microstructural defects may remain in the cured resin. Moisture absorption is increased and mechanical strength is decreased. The use of conventional coupling agents has been practiced, but results are still not adequate. Hitachi Chemical has developed a proprietary interfacial agent that is said to enable high dispersion of the ATH, overcoming these deficiencies and affording high T_g as well [32].

By adding ATH at about 120–160 phr, along with a phenol-formaldehyde (novolac) resin, V-0 ratings can be obtained with good soldering-temperature resistance, according to a Hitachi Chemical patent [33].

Formulations of ATH at above 20 % by weight with improved their thermal stability up to 288 °C have been achieved at Hitachi by use of polysiloxanes [34]. A typical formulation described contains 30 parts of a bisphenol A epoxy (eq. wt. 466), 70 parts of an o-cresol novolac epoxy (eq. wt. 195), 5 parts of dicyandiamide (curing agent), 0.5 parts of 2-ethyl-4-methylimidazole, 155 parts of ATH (preferably < 5 μm average diameter for improved heat resistance), and 4 parts of silicone oligomer solution (preferably a silicone containing a phenyl group for improved heat resistance, and preferably with silanol functionality).

10.4.2 Red Phosphorus plus ATH

Red phosphorus, a relatively stable non-toxic form of phosphorus is available commercially as a powder with added stabilizers and optionally with a protective coating. It is very effective, weight for weight, as a flame retardant, and especially in combination with ATH or $\text{Mg}(\text{OH})_2$. For example, in recent work done at Toshiba, it was shown that V-0 rating can be achieved in laminates made with the blend of bisphenol A and cresol novolac epoxy resins at only 25 wt. % of ATH if 4 wt. % of stabilized red phosphorus is added [35].

More often than in printed wiring boards red phosphorus is used in combination with ATH in molding encapsulation compounds. The amount of red phosphorus in such formulations can vary very much from 3–10 wt. % P_{red} [36] to only 1 wt. % P_{red} + 1 wt. % ATH [37] depending on loading of inert silica filler, which could be as high as 80 wt. %. Red phosphorus stabilized with ZnO or TiO_2 and encapsulated with phenolic resin helps to avoid slow oxidation and hydrolysis of P_{red} [38].

One problem with red phosphorus, aside from the obvious pigmentation, is that it is difficult to handle the powder which is flammable until it is incorporated into the plastic. This problem can be overcome since masterbatches can be purchased (from Italmatch, for example) already mixed with an epoxy resin. There remains the very slow but perceptible attack of

moisture on red phosphorus which produces traces of phosphine (malodorous, toxic, eventually corrosive) and phosphorus acids (corrosive) [37]. Red phosphorus can be stabilized and encapsulated to minimize this problem but there has been still a serious electrical failure rate with some of these products [39].

10.4.3 Other Additive Phosphorus Compounds in PWB

In this book, we attempt to focus on those systems in serious commercial use or development. A broader review of flame retarding epoxies with phosphorus was recently published by Jain *et al.* [40] encompassing many academic or undeveloped additive and reactive systems as well as those which are covered by our present review.

PWB of FR-2 and CEM-1 classifications (phenolic/paper) have for a long time used aryl phosphates, even simple ones such as triphenyl phosphate. The patent literature indicates the use of some phosphorylated novolacs and some more hydrolysis-resistant aryl phosphates such as Daihachi's PX-200®, tetrakis(2,6-dimethylphenyl) resorcinol diphosphate, or an aryl phosphate of this sort along with ATH and a melamine resin [41]. Example of FR-4 laminates are shown in recent Fuji Electronic patents where Asahi Denka ADK STAB® F-500 (analog of PX-200) is used at the level providing 4.4 wt. % phosphorus in combination with 20 wt. % ATH in an epoxy novolac formulation [42]. A V-0 rating is achieved in this laminate. Aromatic bisphosphates are also effective at the low level of 1.5 wt. % in heavily filled molding compounds [43] and are probably finding commercial use there, especially those showing high hydrolytic stability.

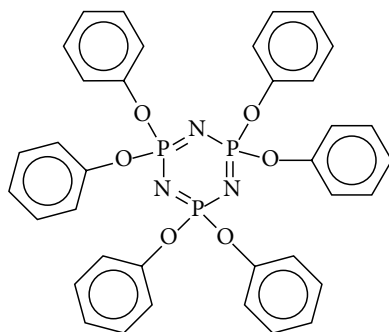
Other thermally stable additives with good flame retardant (char-enhancing) activity and probably with adequate hydrolysis resistance are pentaerythritol bis(benzylphosphonates) developed by Teijin Chemicals [44]. The developmental status of these products is uncertain. One problem with phosphate ester flame retardants is that they tend to be more polar, more water-sensitive, and if they have C–O–P bonds or P–O–P bonds, they pose a risk of hydrolysis under humid exposure conditions. Hydrolysed phosphate esters tend to absorb more moisture and because of this they may perform inferior to brominated systems in the "Pressure Cooker Test". The thermomechanical properties of the PWB, especially glass transition temperature, may also be deteriorated by plasticizer-like additives, such as typical organic phosphates. Although it was believed for years that laminates with higher T_g should have better resistance to thermal shock, recent analysis of lead-free PWBs on the market show that medium T_g laminates may perform as well or better than high T_g laminates if they have the right flexibility and are less prone to cracks [45]. Because phosphorus-containing laminates tend to have lower coefficients of thermal expansion compared to tetrabromobisphenol A, halogen-free laminates may perform better in delamination tests where moisture is not involved [46].

An indication of the shortcomings that may be found with the use of a phosphorus ester is given by a study at Resolution Performance Products, where a non-halogen epoxy laminate (a phosphorus type) is shown to have very high moisture uptake compared to the bromine-containing laminates, and poor solder resistance (20 s at 288 °C) [47].

A high degree of flame retardant efficacy has been found with aluminum diethylphosphinate as an additive in epoxy resins, particularly in combination with alumina trihydrate [48]. The

commercial use of this system in the Far East and in high frequency specialty laminates [49, 50] appears likely. One important feature of this additive is that it does not have C–O–P bonds (it is not an ester), so it is hydrolysis resistant and has little moisture-absorbing tendency.

Hexaphenyltricyclophosphazene (see structure below) has a very low dipole moment and because of this it is advantageous in high frequency low dielectric loss laminates [51]. This flame retardant is manufactured in Japan by Otsuka and the product contains mostly a mixture of tri- and tetracyclophosphazenes. Significant effort by various Japanese companies in attempt to functionalize cyclic phenoxyposphazenes in order to make them reactive with epoxy most likely has not resulted in a commercial product as yet.



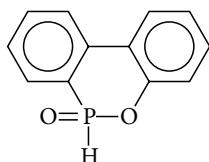
10.4.4 Reactive Phosphorus Compounds in Epoxy Resins

An extensive study by Siemens jointly with Isola led to some formulations that were given market trials for prepregs and laminated PWB and possibly other applications. These are based on reacted-in phosphorus compounds of various sorts, along with melamine structures, but with no filler. The halogen-free DURAVER® E-Cu 156, which may utilize either a reacted-in or added phosphorus, is claimed to have physical properties “virtually identical” to the standard FR-4, made with tetrabromobisphenol A, although the T_g seems to be lower [52]. Some idea of the reacted-in phosphorus compounds in the Siemens project are suggested by patents. For example, a diglycidyl ester of phenylphosphonic acid [53] or propylphosphonic acid [54] is disclosed as a useful reactant, especially for injection molded products. Other patents show reaction of phosphorus anhydrides with the epoxy resin [55, 56]. Besides the phosphorus component, these Siemens/Isola formulations use highly reactive amine components to form a dense three-dimensional network [57].

Dow researchers have disclosed the reaction of epoxy resins with phosphonic esters by an insertion reaction, producing a new ester linkage [58]. They show that this reaction, run concurrent with the cure, to be catalyzed by amines, quaternary ammonium or phosphonium compounds. An example of an effective formulation shows 84 parts of epoxy resin, 14 parts of Rhodia's Amgard® V19 (a cyclic diphosphonate made from trimethylolpropane and dimethyl methylphosphonate), 2 parts dicyandiamide (crosslinker), and 2 parts of 2-phenylimidazole (catalyst). This formulation when cured gives a V-0 rating at 1.7–1.8 mm laminate thickness, a T_g of 146–149 °C and passes the “Pressure Cooker Test” for hydrolytic stability.

Great Lakes Chemical (now Chemtura) announced in 2004 [59] a new phosphorus reactant for epoxies — it is a solid, melting point 200–230 °C, with 9.6–9.8 % P and a hydroxyl equivalent weight of 160–165. It has enough thermal stability to be used for circuit board epoxies which must survive lead-free soldering, and it much provide a high T_g in the cured epoxy. Using this compound, with a phenol-formaldehyde or, even better, a benzoguanidine-co-phenol formaldehyde novolac curing agent, and 48–54 % ATH, a V-0 rating could be obtained. Patents to Chemtura indicate that this product may be a mixture of mono-/di-(4-hydroxyphenyl)phenylphosphine oxides [60]. Actual commercial status of this product is unclear.

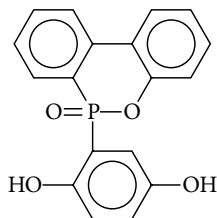
A large number of patent and non-patent citations, both industrial and academic, are found with regard to a dihydrooxaphosphaphenanthrene (DOPO, see structure below). This is a cyclic hydrogenphosphinate made from o-phenylphenol and phosphorus trichloride; the final DOPO has no chlorine but has a P–H bond which when properly catalyzed for example, with a quaternary phosphonium salt [61] can react with epoxy groups. It was originally developed for Toyobo's polyester textile fibers; the hydrogen phosphinate intermediate was attached to a diester and reacted into the polyethylene terephthalate. Since this polyester product was commercial, DOPO was available for other uses. Patents to Japanese, German, US and Taiwanese companies [62–65] show the use of DOPO in epoxies, particularly in PWB. In Japan, it is made by Sanko, in Europe by Schill & Seilacher, and there are also local productions in Taiwan and China. Besides its use as a flame retardant intermediate, DOPO also has applications as an antioxidant-type stabilizer.



In the early formulations containing DOPO it was incorporated in epoxy during the curing process, but later came realization that better properties will be obtained if DOPO is pre-reacted with epoxy [65]. Since DOPO is monofunctional and it consumes one epoxy group, it is usually pre-reacted with multifunctional epoxies, assuming that two or more epoxy groups remained unreacted for further curing. The most preferable resin for prereaction with DOPO is cresol novolac epoxy resin because of inherently lower water absorption compared to other high volume resins. Triazine-modified phenolic novolac LA 7054 produced by Dainippon Ink which is used as a curing agent in the formulation helps further improve hydrolytic stability [66]. Since DOPO always contains a few percent of open phosphaphenanthrene ring structure, the final quality of laminates depends very much on the level of this impurity, the lower the better.

There is very large number of patents and a number of articles from Taiwan and Japan showing procedures where DOPO is first reacted with another intermediate, such as benzoquinone or naphthoquinone, and made into a diol [67] or, by reaction of the diol with epichlorohydrin to form a diglycidyl ether [68]. The product of reaction of DOPO with benzoquinone is manufactured by Sanko and marketed in Japan as HCA-HQ (see structure below). HCA-HQ

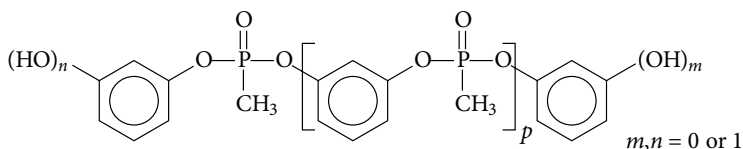
diol is used in a “chain extension” reaction in which it is reacted with an epoxy resin to make a linear epoxy-terminated resin which can subsequently be cured in the usual manner [69, 70]. This extensive technology has been reviewed elsewhere by Weil [71]. These derivatives have advantages over DOPO because they are difunctional and therefore act as “chain extender”, not a “chain terminator”.



Some highly elaborated derivatives of DOPO developed at Vantico are benzoxazines, made by reaction of DOPO with various imines and containing the structure —N=CH—Aryl [72]. These relatively expensive structures when cured to produce PWB laminates are said to favor high T_g and provide passing results in the “Pressure Cooker Test”. In the recent patent to Dow [73] DOPO was condensed with phenol novolac resin which created a phosphorus-containing curing agent. Novolac epoxy laminates cured with this curing agent and DICY showed V-0 rating and relatively high $T_g = 170^\circ\text{C}$.

A study of the mode of action of the various DOPO flame retardants suggested that at least part of their action is vapor-phase flame retardancy due to volatilization of some P-containing fragments, which can scavenge active radicals such as hydrogen atoms in the flame [74]. This same study showed that a simpler phosphorus reactive such as diphenyl phosphite was relatively ineffective.

A high % P (17.5) aromatic phosphonate oligomer, with excellent thermal stability up to about 330°C , has been recently introduced by Akzo Nobel (later Supresta, now ICL-IP) as Fyrol® PMP (see structure below). This is used as a curing agent for epoxy and provides good flame retardancy at as low as 20 % in a phenol-formaldehyde novolac epoxy [75]. The resultant FR-4 laminates pass the “Pressure Cooker Test” and provide boards with a T_g of $145\text{--}170^\circ\text{C}$ [76, 77]. It has been found that the reaction with epoxy groups is not only on the terminal hydroxy groups but is also an insertion into the phosphonate ester linkages [78]. The result is a tightly crosslinked cured epoxy, which accounts for the high T_g . Because of this specific mechanism of curing, the resulting epoxy resin shows very good thermal stability, which is beneficial for lead-free soldering. This reactive phosphonate is also effective in combination with formulations containing an inorganic filler such as ATH [79]. It also decreases peak rate of heat release and smoke in carbon-fiber-reinforced epoxy composites [80]. A Huntsman patent application [81] shows use of this phosphonate oligomer with a benzoxazine coreactant in epoxies.



10.4.5 Use of Metal Hydroxide Additive, Char-Favoring Curing System and Char-Promoter

To avoid the use of both halogen and phosphorus, NEC researchers [82] used a phenolic epoxy with a aminotriazine hardener, zinc molybdate on talc as char promoter and a limited amount of ATH. They were able to obtain circuitboard laminates suitable as replacements for the standard FR-4 tetrabromobisphenol-based product.

10.5 Resin Design for Flame Retardancy

Research in Japan has shown that by modifying the epoxy resin with more thermally stable inflexible structures, such as biphenyl or naphthalene groups between the glycidoxyphenyl groups, and/or nitrogen heterocyclic structures such as reacted-in triazine, oxazoline or oxazine rings, the product can be made to achieve the V-1 level and by also providing supplementary flame retardants such as aryl phosphates and/or ATH, V-0 can be reached [83–88]. Such formulations, designated by Hitachi as BE resins, are mentioned for sealing and encapsulating electronic parts as well as for PWB. By using the new epoxy resin plus modified nitrogen-containing aromatic coreactant with spread-out glass cloth and non-woven glass fabric, PWB can be made with not only flame retardance but also good mechanical properties, laser drilling performance, and cost according to Hitachi Chemical and Motorola [89, 90]. The Hitachi formulations based on 20 % inflexible aromatic resins and no halogen, antimony or red phosphorus are in commercial production and use as of spring 2003 for Motorola's wireless electronic equipment. These formulations are believed to contain additive flame retardants such as phosphorus esters in lesser amounts than would be required with conventional bisphenol A epoxies.

Hitachi formulations for epoxy molding and sealing resins are often very complex; although it is difficult to learn which are commercial, an illustrative formulation [91] uses the biphenyl-type epoxy plus a phenol arylalkyl curing resin (Milex® XL 225), a magnesium zinc hydroxide (Echomag® Z 10), an oligomeric phosphate (Daihachi PX 200), melamine, fused silica, and a triphenylphosphine-quinone adduct (a hydroquinone) plus unspecified "other ingredients". The approach of redesigning the epoxy resin has been pursued at several manufacturers. A wide variety of the modified epoxy resins with rigid groups between the glycidoxyphenyl groups are shown in a Shin-Etsu patent [92]. The use of such resins with high loadings of silica, to make compositions suitable for encapsulation of circuit elements, is shown by Shin-Etsu, Sumitomo Bakelite and NEC [93–95]. Some other examples of combinations of highly charring epoxy resins and highly charring phenolic type curing agents are discussed elsewhere [96–99].

Formulations of this sort with char-forming epoxy resins and char-forming crosslinking agents can be made to form a foamed insulating char layer on the surface when exposed to a flame and can afford V-0 formulations for integrated circuit packaging. When applied in PWB, the glass fiber interfered with the foamed layer, so that ATH (50–55 %) had to be added. PWB made in this way were said to be satisfactory in thermal and electrical properties [100].

Both Hitachi and Sumitomo Bakelite show the use of triazine-modified cresol novolacs as components, along with phosphorus additives such as tetrakis(2,6-dimethylphenyl) m-phenylene diphosphate (PX-200®) [101, 102]. Such formulations are used both as package resins for semiconductors and also for PWB.

By use of a “multiaromatic group” such as a xylylene or naphthalene group between phenolic groups in a crosslinker as well as in the epoxy, plus a high loading of fused silica, a non-halogen non-phosphorus flame retarded molding compound with good heat and humidity resistance can be made, and applied to integrated circuit (IC) molding. The relatively elastic but thermally stable network structure forms a good foam char on the surface when exposed to flame, thus is quite flame retardant. It is also high temperature solder resistant. This resin has been applied to ball grid arrays [103].

Similarly, NEC has shown [104], that the use of an epoxy resin with biphenylene ($-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-$) groups between the phenolic groups, particularly if cured with a benzoguanamine, can provide a high degree of charring and thus flame retardancy without other flame retardants.

10.6 A Multi-Pronged Approach to PWB Formulation – Resin Design, Filler, Interphase Control

Sony has used a high heat resistant high-char-forming epoxy resin, along with a mineral filler at rather high loading, along with an interphase control agent (filler-resin compatibilizing agent, filler deagglomerating agent) to produce multi-layer halogen-free flame retardant PWB. Devices such as Sony’s PlayStation2® have been introduced as “green” products.

Other examples of a multi-pronged approach are the use of a selected epoxy resin with a xylylene group between the glycidylxyphenyl groups along with a triazine modified novolac along with a phosphorus reactant such as DOPO as described by Sumitomo Bakelite [105].

10.7 Flame Retarding Epoxy Coatings

Epoxy resins have been used as the resin binder for intumescent paints and mastics. Classical formulations use ammonium polyphosphate (as charring catalyst), a pentaerythritol (“carbonific”, *i. e.*, char former) and melamine (“spumific”, *i. e.*, blowing agent), these three ingredients typically in about 3:1:1 weight ratio. Formulations based on these or similar components are reviewed in the classical article by Vandersall [106]. Present day formulations can be rather complex, particularly those used for their intumescent thick coatings (mastic) such as employed for protection of off-shore oil drilling platforms and petrochemical installations.

Examples of such advanced and proprietary formulations are Textron's (now Akzo Nobel's) Chartek® and PPG's Pittchar®. An example of a Pittchar® formulation is disclosed in a PPG patent [107] (component; parts by weight): Package 1: diglycidyl ether of bisphenol A, 35.77; melamine, 2.75; ammonium polyphosphate, 4.52; tall oil fatty acid, 4.27; tris(2-chloroethyl) phosphate, 8.79; attapulgite gellant, 3.31; boric acid, 20.64; zinc borate, 7.87; wollastonite, 12.05. Package 2: Versamid® 150 curing agent, 72.25; Aerosil® vapor-phase-produced silica, 3.50; Imsil® A-10 silica, 13.72; attapulgite gellant, 4.50; talc, 6.00. Package 1 and package 2 are mixed in 1.65 weight ratio before applying. This coating is applied in a thick layer as a mastic. A more flexible epoxy coating with many of the same ingredients but with a polyester-chain-extended epoxy has been described in later PPG patents [108, 109].

An interesting intumescent coating for steel has recently been patented and probably commercialized by Chance & Hunt Ltd. and Ferro Ltd. [110], wherein a combination of an epoxy resin with an aldehyde resin or ketone thermoplastic resin serving as part of the binder and as the "carbonific" (char-forming) component. The formulation is: 18 % epoxy resin, 6 % phenolic curing agent, 10 % ketone resin (such as BASF's Laropal® A81), 3.5 % hydrogenated castor oil viscosity modifier (such as Rheox's Thixcin®), 55 % ammonium polyphosphate (such as Exolit® 422) and 7.5 % TiO₂.

A low density epoxy-based intumescent coating, Textron's Chartek® VII, is described in a patent [111]. The components, which must be mixed in a very specific sequence and manner, is quite complex, as shown in Table 10.2. Each of the two parts is mixed before applying by spray equipment.

The density of this coating can be further reduced by pressurizing and dispersing a gas in it before applying. This recipe suggests that sophisticated formulation development is needed to achieve competitive products in the flame retardant coatings field.

Recent intumescent coatings with lengthened fire resistance has made use of the very active dialkylphosphinate aluminum salt as part of the flame retardant composition [112]. A repre-

Table 10.2 Intumescent Low Density Epoxy Coating (Mastic) Formulation

Part 1	
Ingredient	Weight (lbs.)
Epoxy resin (Dow DER 331)	1702.8
Triaryl phosphate	438.3
Black pigment	4.5
Antifoaming siloxane surfactant	0.45
Amorphous hydrophobic fumed silica	67.5
Fire retardant mix (64 % ammonium polyphosphate (Exolit® 422), 36 % tris(hydroxyethyl)isocyanurate)	675
Boric acid	1521.4
Expanded perlite	45
Amorphous mineral fiber (Inorphil®)	22.5
High surface area Al ₂ O ₃ /SiO ₂ fiber (HSA Fiber, Unifrax®)	22.5

Part 2

Ingredient	Weight (lbs.)
Amidoamine curing agent	2554
Wetting agent	10
Antifoaming surfactant	0.4
Milled limestone	401.2
Fire retardant mix (64 % ammonium polyphosphate (Exolit® 422), 36 % tris(hydroxyethyl)isocyanurate)	461.6
Rutile TiO ₂ pigment	76.8
Perlite	224
Amorphous mineral fiber (Inorphil®)	148.4
High surface area Al ₂ O ₃ /SiO ₂ fiber (HSA Fiber, Unifrax®)	123.6

sentive formulation used 25 parts of boric acid, 9 parts of tris(hydroxyethyl)isocyanurate, 2 parts of TiO₂, and 5 parts of a mixture of ammonium polyphosphate and aluminum diethylphosphinate (Exolit® OP 1230) in 100 parts of epoxy resin (Beckopox® EP140) cured with an aliphatic polyamine. Cured on steel at 3.5 mm, this coating gave 44 minutes of fire resistance.

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11 Flame Retardants in Commercial Use or Development for Textiles

11.1 General Background

The demand for textile flame retardancy is mainly in work clothing, firefighter apparel, institutional draperies, institutional upholstery, institutional and commercial carpet, transportation (especially aircraft where blankets and seat covers must pass Federal requirements), military garments, professional racers' garments, and bedding. General adult apparel is almost never flame retarded because of lack of consumer demand and lack of sufficiently stringent mandated standards. Children's sleepwear requirements, once a promising market for flame retardant cotton, are now usually met by choice of thermoplastic synthetic fabrics. A recent development impacting textile flammability has been a US Federal open-flame test requirement for mattresses. Federal requirements for other bedding and upholstered furniture are pending.

Other reviews of this topic can be found as a chapter by Hauser and Schindler in a 2004 book on chemical finishing [1], in chapters by Horrocks in books [2, 3] on fire retardant materials and in an article in the Kirk-Othmer Encyclopedia [4]. Inherently flame resistant fibers are discussed by Bajaj in the Handbook of Technical Textiles [5]. A 2005 review by Horrocks *et al.* [6] is an excellent overview encompassing the scientific research aspects of textile flame retardancy.

11.1.1 A Brief Review of the History of Flame Retardant Textiles

The chemical flame retardancy of textiles has a history going back at least to 1735 where borax, vitreol (a metal sulfate) and some other mineral substances were patented in England for flame retarding canvas and linen [7]. It is worth noting that borax is still often used for non-durable flame retarding of tent fabric, and some sulfates (such as ammonium and occasionally alum) are also used in non-durable flame retardancy. The first systematic study was done at the behest of the French government to flame retard theater curtains, and ammonium phosphate (still used!) was identified as highly effective by Gay-Lussac in 1821. Around the time of World War II, studies were made in military laboratories which covered a wide range of inorganic additives and treatment processes. Much of this work is summarized in an excellent monograph by Little [8], which is still of value particularly to avoid the repetition of old work. Useful discussions of textile applications are also found in Lyons' monograph on flame retardants [9].

In the mid-20th century, serious work was done to durably flame retard cotton garments at Albright & Wilson (UK), Hooker Chemical Co. (Niagara Falls, NY), the US Department of Agriculture Southern Regional Research Laboratory (New Orleans, LA) and American Cyanamid Co. (Stamford, CT) and in Europe at Ciba. One driving force was the need to

flame-retard cotton work clothing, and another, later, was the Federal children's sleepwear regulation.

11.1.2 Flammability of Textiles (General Comments)

There is a great variety of textiles in use which differ widely in construction (knitted, woven, and many types of nonwovens) and in the chemical nature of the fibers. Because of this, the flammability of textiles varies dramatically from very flammable cellulosic and common synthetic fiber textiles to inherently flame retardant textiles (discussed later in this chapter). Clothing worn by people does not often ignite, but if it does, the result is a high rate of fatalities (almost one of every four such accidents) or disfiguring burns, especially with nightwear [10]. On the other hand, fires resulting from upholstered furniture, floor coverings, curtains and drapes are more frequent, but result in a significantly lower rate of fatalities. The flame spread rate observed after ignition of cellulosic, common synthetics and blended fabric apparels is heavily dependent on fabric areal density, with the highest danger with light weight fabric as shown by Hirschler *et al.* [11, 12].

Apart from low areal weight fabrics, raised-surface (highly brushed) apparel is also of concern from the point of view of high flammability hazard, because of easy ignition and fast flame spread. In order to pass the General Wearing Apparel Standard (GWA, Title 16 CFR part 1610) cotton is usually blended with 10–20 % of polyester fibers. Although there is significant consumer demand for all-cotton raised-surface apparel there is no commercial FR treatment available which satisfies durability and allows keeping the aesthetics of the garment according to a Cotton Council report (2002) [13].

11.1.3 Modes of Action

A detailed discussion of mode of action is outside the scope of this chapter and the reader is referred to reviews published by the authors [14, 15]. At the risk of oversimplifying a complex subject, halogen and halogen-antimony systems tend to be flame inhibitors, the phosphorus and boron systems tend to enhance charring and formation of surface barrier layers, and the metal hydroxides tend to be endothermic water-releasing systems. In thermoplastic textiles, such as PET, some of the additives also aid extinguishment by melt flow enhancement. Otherwise, many inherently flame retardant fibers and fabrics are those which form a char on fire exposure.

11.1.4 Detrimental Effects on Flammability

Components of fabrics, such as 100 % polyesters, in which melt flow is part of their mode of extinguishment can be made more flammable by traces of silicones [16], which probably burn to silica and then act as a wick. Some print pigments can also have a detrimental effect on polyester flame retardancy [17]. Some disperse dyes were shown in a Turkish study [18] to have a significant adverse effect on the flammability of PET textile, increasing flame spread speeds by approximately 100 %.

Combinations of flame retardant thermoplastics with flame retardant non-melting components at the fiber or yarn level of blending, as sewing thread, or as layered fabrics can often be much more flammable than the individual components. This is due partly to a “wick” effect but other causes may be involved. For example, thermolysis of cotton-polyester blends can give more flammable vapor than either alone [19].

11.2 Non-Durable Treatments

11.2.1 Non-Durable Treatments of Cotton and other Cellulosics

Non-durable flame retardant treatments are those which will wash off readily with plain water. They will usually resist dry cleaning with non-aqueous solvents. These finishes are most often used for disposable goods, examples being disposable medical gowns, party costumes, and sometimes wall covering, either cloth or paper. They can be used on work clothing and curtains, but the laundry then must reapply them after each wash. The treatments are usually applied by padding or spraying of an aqueous solution.

As mentioned, ammonium phosphates are effective at add-ons in the range of 1–2 % phosphorus content relative to the weight of the fabric to provide self-extinguishing cotton. Either mono- or diammonium phosphates can be used. A maximum of water solubility can be achieved by using a mixture of both. When the aqueous solution dries, after application by dipping and squeezing (dip and nip), small crystals of the phosphate salt may form and may present a gritty tactile sensation or “hand”. Commercial formulations exist where a small amount of an additive, such as an organic acid phosphate ammonium salt, inhibits the crystallization and gives a more flexible, or at least less gritty, hand.

A number of commercial formulations are sold for application by the finishing plant, commercial laundry, or even individuals. Many of these have surfactants to speed up wetting and aid penetration into the lumen of the hollow cellulose fibers. Such penetration will probably result in a better hand than superficial application. Urea is often added to aid cellulose swelling as well as to enhance flame retardancy.

A number of proprietary ammonium phosphate salt formulations are widely used. Water-soluble lower molecular weight ammonium polyphosphate is also used and probably has a hand advantage since it does not crystallize readily. In view of the mode of action (cellulose dehydration and charring), it can be expected that the polyphosphate would also be somewhat more efficient than the (ortho)phosphates. Ammonium bromide can also be used in combination with ammonium phosphates to provide some vapor-phase flame retardant action, particularly helpful when the textile to be treated is a synthetic or blend. Ammonium sulfamate or sulfate is also included in some ammonium phosphate formulations. An enhancement of efficiency is often found with such sulfur-phosphorus combinations [20].

The high molecular weight substantially water-insoluble ammonium polyphosphate, available as a powder, can also be used but in this case it must be formulated as a suspension or slurry, typically with an acrylic binder, and for further water-resistance, sometimes with a melamine-formaldehyde resin coating [21] and also with glass microspheres [22]. This treatment is applied, typically as backcoatings, to curtains, awnings, carpets, upholstery, bedding

and the like. A further use of insoluble ammonium polyphosphate is in intumescent coatings, discussed further below. Ammonium polyphosphate is reviewed in depth by Horrocks [3].

Diguanidine hydrogen phosphate or monoguanidine dihydrogen phosphates are also examples of inexpensive phosphates for non-durable cotton treatment [23]. Cotton padded with diguanidine hydrogen phosphate provides an M2 rating in the French electrical burner test FD P 92-507. Monoguanidine dihydrogen phosphate is even more effective and an M1 rating is achieved. However, after the water soaking test, the treated samples fail the flammability tests, so they must be counted as non-durable. Baking after padding and drying can afford a semi-durable result.

As mentioned in the historical discussion, the use of borax (sodium borate) as a flame retardant for cellulose is still practiced. Since borax is available everywhere for laundry use, it is a mainstay of do-it-yourself flame retardant treatments, such as for canvas camping tents. Obviously it is not resistant to rainfall or to washing. A less alkaline borax-boric acid mixture is also used.

Some low cost water-soluble organophosphorus compounds sold as non-durable or semi-durable treatments are probably salts of non-odorous amines such as ethanolamines, guanidine or the like. The formulations are generally proprietary.

11.2.2 Non-Durable Treatments for Polyester

A pH-adjusted mixture of guanidine phosphate and amidosulfonic acid has been developed by Ciba for treatment of polyester fabric [24]. It is said to be more effective than guanidine phosphate by itself. Sulfur compounds are often found to activate phosphorus flame retardants [20].

11.2.3 Semi-Durable Treatments for Cotton

These treatments will survive water soaking or leaching to various degrees, but generally will not survive laundering, or only a very few launderings. One version comprises salts of low solubility. The removal of such finishes occurs even with plain water. A typical test is the BS 5852 standard where the fabric is soaked for 30 minutes in water at 40 °C (BS 5651 conditions) [25].

Other versions of semi-durable treatments are ones which are reacted onto the cellulosic fabric but lose activity by ion-exchange with alkaline detergents and/or hard water. It has long been known that heating cellulose with phosphoric acid or ammonium phosphates to temperatures where evolution of water occurs will produce a cellulose phosphate, by phosphorylation on the HOCH₂-groups (the 6-hydroxyl) of the glucose units. Damage is done to the cellulose — it becomes degraded and weakened by acid-catalyzed hydrolysis. Cotton fabric loses its tear strength and becomes yellow to brown. Buffering the acidity of the treatment can reduce the damage.

It was found in the 1940s that if urea is applied to the fabric along with the phosphoric acid or ammonium salt, the phosphorylation proceeds more gently and tolerably useful flame-retarded cotton fabric can be obtained, not discolored or only slightly discolored. Some, but

not all dyes, can survive this treatment. With the phosphoric acid groups chemically attached and neutralized to a degree by ammonium cations, the finish can be fairly durable to water washing. Later, it was found that even less damage or discoloration is done if, instead of urea, dicyandiamide is used as the coreactant. A dicyandiamide (or actually guanylurea formed by hydration of the cyano group) salt of phosphoric acid is commercially available and in use for this purpose and also used in wood flame retardancy. A recent Milliken patent [26] shows the treatment of cellulosic fibers with ammonium polyphosphate plus urea, with heating to 140–200 °C, and then forming the treated fibers into a nonwoven textile with leach-durable flame retardant properties.

Semi-durable finishes are not durable to alkaline laundering conditions, which destroy the flame retardancy partly by cleavage of the phosphate-to-cellulose bonds and partly by ion-exchanging sodium cations for acid hydrogen or ammonium. The sodium cellulose phosphate structure, while not totally devoid of flame retardant action, is a poor flame retardant because the effective phosphoric/polyphosphoric release on burning, necessary for the char-forming mode of action, is partly or totally defeated by neutralization and buffering by the sodium salt. If the laundering is in hard water, Ca and Mg cations can also be collected by the phosphate groups and further spoil the flame retardant action by the same mechanism. Finishes thus deactivated can sometimes be restored at least partly to activity by an acid treatment (sometimes called a “laundry sour”, often using oxalic acid) to remove the alkali or alkaline earth cations.

11.2.4 Further Development of the Phosphorylation of Cellulose

By using an organic phosphonic acid such as $\text{CH}_3\text{PO}(\text{OH})_2$ instead of phosphoric acid, a finish with less sodium ion-exchange and calcium ion-capturing tendency can be obtained. Here, the favorite nitrogen base is once again cyanoguanidine. Ciba's Flovan® CGN is believed to be the cyanoguanidine (or possibly guanylurea) salt of methylphosphonic acid. Combinations with boric acid and urea are even more effective as shown by Ciba researchers [27]. The textile may be merely dried to obtain a non-durable finish, or optionally may be cured to obtain semi-durable flame retardancy.

Guanidine phosphate can also be used in this type of treatment. Some proprietary semi-durable treatments are available, and have been formulated probably with buffers and wetting agents to give less yellowing, less damage to the fabric and more acceptable hand. An example is Flammentin® FMB (Thor Specialities). It is a water-soluble material applied by padding, foaming or exhausting, followed by drying and baking for about 5 minutes at 150 °C. It will provide flame retardancy which can survive the water-soak requirements of the British upholstered furniture standard [28].

Pyrovatim® PBS is a semi-durable flame retardant introduced by Ciba and now marketed by Huntsman. It is a phosphorus-based product that can be used either as non-durable or soak-durable. To achieve the soak-durable result, the treated fabric should be cured at 160 °C for 160 seconds or 170 °C for 90 seconds, based on a detailed study [29]. Pyrovatim PBS has high whiteness and non-dusting characteristics, and is said to be suitable for interliners, upholstery, curtains and protective garments. Although the structure of Pyrovatim PBS seems not to have been published, it may be noted that recent patent applications of Ciba [30] show

salts of polyethyleneimine with aminoalkylphosphonic acids as semi-durable finishes. These are only examples of many semi-durable finishes which are available or described in patents.

11.3 Backcoating with Phosphorus-Containing Formulations

A semi-durable approach is the use of a backcoating the durability of which depends largely on the binder and the hydrolytic stability of the flame retardant. The very widely used decabromodiphenyl ether-antimony oxide formulations which are effective on many different fabrics are discussed further below. The phosphorus-based backcoatings are more limited to cellulose which can char. Formulations using ammonium polyphosphate plus, optionally, additional char formers such as pentaerythritol have been shown to be effective backcoatings on cotton by Horrocks [31]. If greater resistance to hot water washing is needed, coated ammonium polyphosphates such as Clariant's Exolit® AP 462 or Budenheim's FR CROS® 486 and 487 may be used. An even more tightly coated version is Budenheim FR CROS® 489, which has a melamine-reacted crystal surface and is also melamine-formaldehyde resin coated. Commercial treatments of this sort have been marketed as "more environmentally friendly" replacements for the decabromodiphenyl ether backcoating which comes under criticism by environmental activists.

Phosphorus-containing coatings can be formulated to perform as intumescent, which form a barrier of foamed char when exposed to a flame. The intumescent material also closes up the interstices of the fire-exposed fabric. The use of intumescent barrier coatings for textiles has been reviewed briefly by Cox [32] and a scientific assessment of the function of intumescent in textiles has been published by Kandola and Horrocks [33].

An example of an intumescent, a typical ammonium polyphosphate-pentaerythritol-melamine-binder formulation, is shown in application to fabric from core-spun yarn in a Springs patent [34]. Cost and performance considerations have been reviewed by Dombrowski [35]; coated fabrics are said to have a cost advantage over fabrics made from inherently flame retardant fibers. An intumescent coating on Basofil® (an inherently flame retardant fiber discussed further below) gave synergistic results in regard to flame breakthrough time.

The choice of binder in formulating an intumescent coating for textiles is important. Acrylics are typically used. To avoid a setback in flame retardancy, the use of a vinylidene chloride/acrylic latex is shown in the Springs patent [34]. A commercial dispersion of this type is Aflamman® NAH from Thor Group Ltd., UK.

A wide variety of commercial phosphorus-based products available for fabrics backcoating was studied by Bolton (UK) researchers [36]. The effectiveness of phosphorus-based intumescent backcoatings, particularly those based on ammonium polyphosphate, has been shown to be favored by the melting and penetrating of the intumescent material through to the face of the fabric [37]. Further efficacy is achieved by including a volatile phosphorus-containing flame retardant such as Antiblaze® CU, Fyrol® 51 or tributyl phosphate in the backcoating [38].

Carpets with enhanced flame retardancy can be made by placing an intumescent layer between the tufting and the backing, or on the upper surface of the backing. Since washing carpets is infrequent, even soluble phosphorus compounds can be used below the tufting but

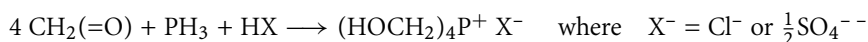
some US manufacturers prefer to have some wash durability or even laundering durability. A patent application [39] exemplifies use of a combination of ammonium phosphate (soluble salt), melamine cyanurate and ATH plus an acrylic binder. Another patent to Akro Fire-guard Products [40] suggests use of the classical intumescent combination of ammonium polyphosphate, pentaerythritol and melamine in carpet backing. Nylon carpets made with this backing are fire retardant and are said to meet airline standards for fire safety.

11.4 Durable Finishes

11.4.1 THPX Finishes for Cellulosics and Blends

The leading commercial product, with about a 50-year history but still subject to improvements, is that based on tetrakis(hydroxymethyl)phosphonium salts. This type of finish was originally developed by Albright & Wilson in the UK with a parallel project at Hooker Chemical in Niagara Falls, NY and much basic research by the US Department of Agriculture Southern Regional Research Laboratory in New Orleans. A review of the basic chemistry was published by USDA-SRRL researchers [41].

The chemistry is based on a reactive product made from addition of formaldehyde to phosphine (made as a main product by an Albright & Wilson/American Cyanamid process from phosphorus, or obtained as a byproduct of manufacture of sodium hypophosphite from phosphorus and alkali). In the presence of acid, usually hydrochloric or sulfuric, the reaction is:



The tetrakis(hydroxymethyl)phosphonium salt is a water-soluble rather storage-stable compound. It should be noted that there is no hydrolyzable linkage in these salts. Both the chloride and the sulfate are on the market. The chloride had some concern associated with it because small amounts of free or loosely bound formaldehyde in the technical product were suspected of being able to form bis(chloromethyl) ether, a volatile carcinogen, which must be avoided in the work space.

There is a rich literature on ways to react these phosphonium salts, plus many kinds of ureas, melamines, *etc.* with cellulose. A long series of articles by Nair [42–45] surveys many aspects and variants of this type of finish.

However, it appears that the commercially successful way of using the THPX chemistry is focused on the Proban® process, a trade-marked process formerly belonging to Albright & Wilson, and now Rhodia Consumer Specialties. In this process, as described by Cole [46], THPC or THPS is prereacted with urea and the solution then adjusted to pH 5–8 before padding onto cotton. An improved procedure for this step, avoiding formation of insolubles, is described in a later patent by Cole and Stephenson [47]. The impregnated fibers are then dried and treated with gaseous ammonia in a specially designed “ammoniation chamber” which cures (crosslinks) the finish. At this point, the structure of the finish is probably mainly a network of N—CH₂—P linkages where the phosphorus is still in the lower (organophosphine) state of oxidation. It can be stored in air to allow the phosphorus to become oxidized to the very stable phosphine oxide, or more practicably, treated

with aqueous hydrogen peroxide to rapidly accomplish the same oxidation. The end result is almost certainly a network of $\text{N}-\text{CH}_2-\text{P}(=\text{O})-$ linkages with some of the nitrogens being triple branches and others being the N atoms of the urea units. An idealized unit might be $-\text{NH}-\text{C}(=\text{O})-\text{NH}-\text{CH}_2-\text{P}(=\text{O})(-\text{CH}_2-\text{N}-)_2$. The key fact is that the end product has no hydrolyzable links adjacent to the phosphorus, which is entirely in the stable phosphine oxide structure. As a result, it is a finish durable to 100 industrial launderings with alkaline detergent. The durability was shown by LeBlanc [48] to exceed that of a competitive cotton finish. Cotton fabric with the Proban® treatment is sold as Westex's Indura®, Banwear®, FR-7A®, and Ultrasoft® as well as under private labels. For work clothes, it competes with DuPont's Nomex® aramid (discussed later) and is said to have comfort advantages. It is also used on cotton goods for military applications, hotels, nursing homes and institutions. The finish also has antimicrobial effects.

There are other favorable features. The cure is done gently on the alkaline side so there is very little damage to the cellulose. There is also practically no chemical reaction with the cellulose so that a fairly soft hand and fairly good stress-relieving flexibility of the yarn is maintained, which is favorable to maintaining good tear strength. When the treated fabric is exposed to flame, it chars and does not melt or exhibit flame spread.

A limiting feature for this process is the requirement for a special gas-tight ammoniation chamber that few textile finishers have. In the US, the leading finisher equipped and experienced in running the Proban finish is Westex (Western Piece Dyers) in Chicago, although several other finishers now have and operate the equipment. The Proban finish has been extensively used on work clothes such as steelworkers' and welders' garments. In 2000, Carter's introduced children's cotton sleepwear with the Proban finish. These garments allow for a comfortable loose fit while complying with the Federal Children's Sleepwear Flammability Standard.

A somewhat adverse feature of this process is that the range of cotton dyes is limited and generally vat dyes, which are compatible with the reducing and oxidizing conditions, must be used.

Some process details of the ammoniation and oxidation steps can be found in a USDA publication [49] which however deals with the earlier version of the process (the "THPOH-NH₃ process") before the urea precondensation step was described by Cole. The "THPOH-NH₃ process" was also described in a patent by Hooker inventors [50] with partial drying pointed out as a critical factor for improving fixation. This variable and others in the ammoniation step were further discussed by American Cyanamid researchers [51].

With specific reference to the Proban finish, Dombrowski [52] states that drying should be done to about 18 % moisture before ammoniation (so as to have the insolubilized product well distributed). He also points out that in the oxidation step, cooling is needed and the oxidizing bath should have continuous feed of hydrogen peroxide. In the final wash, several wash boxes are used to bring the fabric to a final pH of 6–8. He states that the process can be applied to nonwovens with some equipment modifications. Unlike wovens, where a tenter frame can be used to carry the fabric through the oven and avoid shrinking, in the nonwoven area it is more important to rely on temperatures that will allow only minimum shrinkage.

The rate of drying and the mode of drying is also important and affects the distribution of cured material and thus the hand of the fabric. Heating by steam cans on both sides of the fabric and rather slow drying is said to be preferable.

A further improvement in the Proban process, shown in an Albright & Wilson patent [53] is to dry the fabric to, preferably, 17–23 % moisture level after the impregnation and then to “batch” the fabric after ammoniation for at least an hour before the oxidation step. This is said to give a higher fixation of the finish. Many other details of the optimum operating conditions for the drying and ammoniation step are given in another Albright & Wilson patent [54].

The same or similar gaseous ammonia cure chemistry is practiced in Europe with Thor’s Aflammit® P [25].

A two-step process where, after the ammoniation to cure the THPC-urea precondensate, another flame retardant application is carried out. This is claimed by Burlington inventors [55] to give a more pliant hand.

11.4.2 Improvements and Recent Developments in the THPX Type of Finish

Blends containing a major percentage of cotton, such as the 80:20 cotton/polyester can be treated by the THPX finish, but results of the unmodified process with a higher polyester blend are usually unsatisfactory.

Blends of 88 % Proban-treated cotton and 12 % high tenacity nylon are sold by Westex as Indura® Ultra Soft fabric, for high comfort work clothing. Related blend fabrics are sold by Mount Vernon Mills. Specific methodology for treating similar cotton-nylon blends with a THPX-urea-ammonia finish is described in a patent [56]. Combinations of cotton and as much as 35 % nylon may require inclusion of a cyclic methylphosphonate flame retardant such as Antiblaze® 19 (subsequently marketed as Antiblaze® CU/CT (Albright & Wilson) or more recently Amgard® CU/CT by Rhodia) in the formulation to flame-retard the nylon [57], and perhaps a second step of THPX-urea-ammonia treatment plus the methylphosphonate [58].

A similar combination can be used to flame retard cotton-polyester blends [59] and this can be done simultaneously with dyeing [60]. An alternative to the cyclic methylphosphonate is application of a suspension of hexabromocyclodecane to the ammoniated THPX treated blend, followed by heating to 360 °F (182 °C) for 45 seconds [61].

Durable flame retardant treatment of cotton-nylon blends using the THPX-gaseous ammonia process within certain process parameters has been disclosed by Fleming and Green [56].

11.4.3 New Products Using the Proban Treatment

A softer version of the Proban treatment has been developed where a long chain fatty amine, such as hydrogenated C_{16–18} tallow alkylamine, is used in small amounts to react with the THPX in the same chemical manner as urea presumably prior to application to the textile and ammoniation [62].

A quilted insulation fabric FlameQuilt® designed as a flame barrier (used as batting) for firemen’s turnout gear has been introduced by Westex using an Indura® (Proban-treated) cotton face fabric with Basofil® and flame retardant rayon blend fiber filling. A related product

ModaQuilt® is modacrylic batting with a Proban-treated cotton facecloth. A softer version of Proban treated cotton is suggested for blending with polyamide imide Kermel® fibers at 70 : 30 ratio [63].

Cotton covered pillows and duvets made with Proban-treated cotton are now being offered, which can pass the British standard for the ignitability of bedcovers and pillows by smoldering and flaming ignition sources, BS 7175:1989 with source 5, a stringent requirement.

By use of two steps of padding, squeezing and gaseous ammonia cure, a flame retardant viscose rayon product has been developed which has a graded concentration of the THPOH-urea finish, higher on the outer portion of the yarn and lower on the inner portion; this fabric is said to be suitable for close-fitting protective garments [64]. Progress has also been made in using the THPOH-urea-ammonia treatment to make protective garments meeting NFPA's Hazard Risk Category 2 with a single layer of 6.25 oz (210 g/m²) cotton knit. These products appear to be commercially available from SSM.

11.4.4 THPX Processes not Using Gaseous Ammonia

Since the ammoniation chamber is not available in most textile finishing plants, consequently much effort seems to have been expended on THPX processes not using gaseous ammonia. It is not known to the authors whether any of these have been commercialized, despite the copious literature which has been reviewed, for example by Nair [42–45].

One version of such a treatment using aqueous ammonia is a method patented by American Cyanamid [65] wherein the fabric after treatment with aqueous ammonia plus thickener is rolled up and held for a prolonged time.

A conventional pad-dry-cure process which achieves durable flame retardancy and wrinkle resistance was described in detail by USDA researchers [66].

11.4.5 Pyrovatex® CP and Similar Competitive Products

An early study on this product is by Ciba-Geigy authors [67]. The principal molecule in Pyrovatex® CP is (CH₃O)₂P(=O)CH₂CH₂C(=O)NHCH₂OH. Its Chemical Abstracts name is phosphonic acid (3-{[hydroxymethyl]amino}-3-oxopropyl)-, dimethyl ester although more generally it is often called N-methylol dimethyl phosphonopropionamide. It is made by methylolation of the dimethyl phosphite adduct of acrylamide. It is a water-soluble product with a mild formaldehyde odor. The article of commerce is not a pure compound — it contains some components with more loosely bound formaldehyde.

A published study on the product refers to the impurities and storage behavior of this product, which seems to be prone to self-condensation reactions [68, 69]. Successful efforts to lower the formaldehyde release are described by Horrocks and Roberts [70].

Pyrovatex CP, the main component being monofunctional, has the capability of reaction with cellulose under acid-catalyzed conditions to produce “aminal” linked structures, of the type mostly on the 6-hydroxyl groups of the cellulose, without crosslinking. The structures produced would be (CH₃O)₂P(=O)CH₂CH₂C(=O)NHCH₂O—CH₂-(6-position of the cellulose glucose units). However, under reasonably accessible finishing conditions with

acid catalysis, the phosphonopropionamide group is not efficiently fixed. Therefore, it is normally used along with an amino resin to achieve a greater level of fixation to the cotton. Recommended aminoplasts have been partially methylated tetra- or pentamethylolmelamine or trimethylolmelamine.

Improvements in the product were made to reduce the amount of loosely-bonded formaldehyde structures. Prof. Horrocks' laboratory (work cited above) and Ciba introduced a LF (low formaldehyde) grade of Pyrovatex CP. Both Pyrovatex® CP and CP-LF have qualified for the European Oeko-Tex environmental standard.

An N-methylol dialkyl phosphonopropionamide similar to Pyrovatex CP is Thor's Aflammit® KWB, which is claimed to have evolved by using HPLC analytical results to a much purer product which can give increased fixation levels, thus minimizing wastage and lessening water pollution [28]. The phosphoric acid catalyst level and the required curing temperature can also be lowered (to as low as 125 °C), with less volatiles in the work space, and with less strength loss and shade alteration of the cotton.

It was shown with Pyrovatex CP or Aflammit KWB that inclusion of a selected nitrogen resin can increase the phosphorus fixation. For example, the % P on cotton after 5 minute cure at 150 °C was 1.76 %, with a glyoxal resin was 1.88 % and with a melamine resin it was 1.98 %. The nitrogen resin also can be expected to provide a boost in flame retardancy and laundering durability.

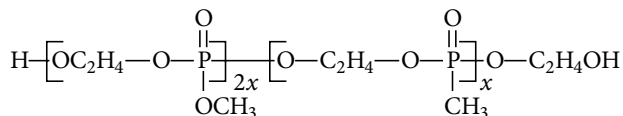
A problem often noted with the N-methylol dialkyl phosphonopropionamide flame retardant for cotton is tar formation in the curing oven. This can be minimized by lowering the cure temperature, increasing the catalyst level, filtering out volatiles in the oven air with an acidified filter cloth, and reducing circulation of air in the curing oven.

Acid hydrolysis on storage, which has been reported with this type of retardant finish [71] can be minimized by careful neutralization of the fabric after curing. Some less well-optimized versions of this finish were found to badly deteriorate the tear strength of cotton, probably by residual acid attack on the moist cellulose. More recently produced finishes with N-methylol dialkyl phosphonopropionamide have been much improved [28] in regard to strength retention. A properly-cured cotton textile with the Pyrovatex CP finish can survive 50 or more launderings, but it is still not as durable as the Proban type of finish and is more sensitive to hypochlorite bleach treatment.

Besides loss of phosphorus during launderings, another problem is the accumulation of alkali metal cations from the detergent and hard water cations (Ca and Mg) probably held by ion exchange on the phosphonic acid groups generated by hydrolysis of the methyl ester groups. As in the case of the semi-durable finishes discussed earlier, this problem can be alleviated by use of soft water, and the flame retardancy effect may also be partially restored by an acid "sour" treatment.

11.4.6 Other Durable Finishes for Cotton

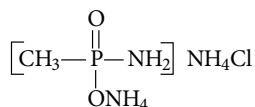
A phosphorus-rich oligomeric alcohol-terminated methylphosphonate-phosphate, Akzo Nobel's Fyrol® 51, also later named as Fyroltex® HP, having the following structure:



has been shown by studies at Akzo Nobel and University of Georgia [72] to be curable on cotton or blends by use of aminoplast resins, in particular (DMDHEU, the common durable press reagent) and trimethylolmelamine, to obtain a flame retardant finish durable to at least 25 home launderings. The finish appears to have an advantage of low formaldehyde odor, and low damage to fabric strength. Based on research at University of Georgia, this type of finish also shows promise on cotton-nylon [73, 74]. Finishes using this phosphorus oligomer have shown promise in finishing plant trials.

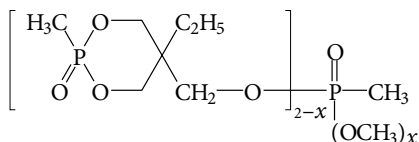
This phosphorus oligomer can also be used in non-formaldehyde finishes where the bonding to cellulose makes use of ester linkages derived from a polycarboxylic acid such as butanetetra-carboxylic acid or citric acid [75, 76].

Recently, a UK based company Isle Firestop Ltd. introduced Noflan®, a phosphorus-chlorine based product which is presumably a mixture of the ammonium salt of methylphosphonoamidic acid and ammonium chloride (see structure below) [77]. This development is based on established Russian technology. Although the product is water soluble, it can be cured with melamine-formaldehyde resin and urea, so it can survive multiple launderings. It is recommended for use in plain cotton or polyester/cotton blends [78]. Real commercial status of this development is unknown, however we believe that it has had some limited success in Europe.



11.5 Thermosol Flame Retardant Treatment of Polyester Fabric

An early version of this method involved the use of tris(dibromopropyl) phosphate but after a short time in the 1970s, this compound was removed from the market when it was found to be mutagenic and possibly carcinogenic. Since then, the major product used in the thermosol treatment of polyester fabric has been a liquid phosphonate (Rhodia's Antiblaze® 19 or Amgard® CU, or Special Materials' SMC 688) of the following structure:



In the product used in the thermosol treatment, x in the above formula is 1. A related triphosphonate (x equal to zero in the above formula; Antiblaze® 1045) can be used as a melt additive in PET fiber prior to spinning. Either phosphonate, once in the PET fiber, is quite resistant to laundering.

In Europe, this diphosphonate product is also available from Thor as Afflamit® PE. Probably Flammex® DS from Zschimmer & Schwarz (Mohsdorf, Germany) is the same or a similar product. Some of the commercial products may contain proprietary wetting agents and perhaps penetrating aids.

The process, briefly reviewed by the present authors [79] involves applying the phosphonate by aqueous padding, then after drying, heating the fabric to about 190–210 °C for about 30–40 seconds. The fibers “open up” (soften and become permeable) and the phosphonate migrates into the fibers. On cooling, the flame retardant is tightly held. Usually the fabric is then washed to remove any surface material. This process is similar to the thermosol dyeing using disperse dyes and indeed the dyeing and flame retarding can be combined. It is said that the color yield of disperse dyes (due to better penetration) can be improved by the phosphonate treatment. Injection of superheated steam into the oven is said to improve penetration and to permit somewhat lower temperatures for the treatment.

This same process is said to be difficult to apply to polyester nonwovens. At the high temperatures required for the thermosol process, severe shrinking will occur, and unlike wovens which can be held in a tenter frame, it is difficult to avoid unacceptable shrinkage [52]. As an alternative, a wash-durable dispersion of decabromodiphenyl ether plus antimony oxide plus an emulsion polymer binder can be used.

It is said that the thermosol process with the diphosphonate can also be applied to wool, wool/polyester or wool/nylon blends.

A thermosol treatment of polyester fabric can also be done using hexabromocyclododecane (Chemtura's CD-75PM®) applied as an aqueous suspension or emulsion, drying and then taking the fabric to 180–205 °C for a short period, thereafter removing excess flame retardant by washing or scouring. A loading of 8–11 % will allow passing the NFPA-701 flammability test and the treated fabric is flame-retarded after repeated launderings.

A solution of hexabromocyclododecane dissolved in the cyclic diphosphonate is available from Special Materials Co. as SMC FR-BM, and this permits a clear thermosol finish at a somewhat lower temperature than needed with HBCD alone. This finish is said to be effective not only on polyester but on low melting fibers such as polypropylene and also on nylon.

11.6 Nylon Topical Finish

A thiourea-formaldehyde oligomer precondensate, with a representative chemical structure of $\text{NH}_2\text{C}(=\text{S})\text{NH}[\text{CH}_2-\text{NH}-\text{C}(=\text{S})\text{NH}]_n\text{CH}_2\text{OH}$ plus an acid catalyst can be applied as an aqueous solution in a padder and cured at moderate temperature to obtain a fairly wash-durable finish which probably has a crosslinked resin structure, with possibly some binding to the amide groups of the nylon [52]. This finish probably works by stimulating melt flow and drip. It is or was commercially available as Sybron's Flamegard® 908.

11.7 Wool

Wool is normally quite slow burning, and in some constructions, wool felt is even claimed to serve as a fire resistant layer [80]. However, for some uses, such as aircraft seating, it needs to be flame retarded. A system developed by Benisek at the International Wool Secretariat uses a treatment with either a soluble hexafluorotitanate or, preferably from a color standpoint, a hexafluorozirconate (the Zirpro® treatment). This system causes formation of intumescent char. Tetrabromophthalic acid or its salts can also be used, although conducive to smoke on burning and not as durable to washing. Benisek showed that the combination of Zirpro and tetrabromophthalate was synergistic [81]. Both the Zirpro and the tetrabromophthalic systems are in commercial use. Aircraft seating is one application.

Recent patent applications of Huntsman Textile Effects (previously Ciba Specialties) [82, 83] describe water-wash-durable flame retardant finishes, shown to be especially suitable for wool and wool blends with nylon or polyolefins, using a salt of polyethyleneimine and an aminomethylphosphonic acid. These were also mentioned earlier as semidurable, the wash durability depending on the blend.

11.8 Processes with Broad Application for Synthetics and Blends

Almost all fabrics can be flame retarded by a sufficiently heavy application of a brominated flame retardant in finely-divided form with a binding agent. An early version of such a system was patented by Mischutin in 1982, covering the use of a brominated water-insoluble solid, especially decabromodiphenyl ether or hexabromocyclododecane at a particle size under 10 (preferably under 2) microns, plus a wetting agent plus a “protective colloid” (such as carboxymethylcellulose) applied at a high concentration as a print paste in the manner of a disperse dye, and heat set [84].

Related systems, often with antimony oxide as a synergist, and with a binder resin, have been widely used on a wide variety of fabrics, natural, synthetics and blends. Decabromodiphenyl ether, being relatively low in cost, has been the usual choice. Obviously, application on the face of the fabric produces a white coating with a propensity to undergo photochemical discoloration, so that a frequent method of using such compositions is as a backcoating, applied by knife coating, doctor blade, kiss roll, foaming or spraying. For complete coverage of both faces, immersion and drying can be done. Typical add-ons of decabromodiphenyl ether use a 2:1 weight ratio with antimony oxide on a polyester fabric at about 10–25 % by weight of total flame retardant relative to weight of the fabric, usually bonded by an acrylic latex. Such backcoatings are effective on a wide range of fabrics, including nylon, polypropylene, polyester-nylon blends, acrylics, and many blends.

Important applications are in automotive upholstery, draperies for hotels and public buildings, and institutional upholstered furniture. The relations of fabric weight and type to add-on, and use of some alternative brominated flame retardants such as hexabromocyclododecane (photostability advantage) were discussed by Rose [85].

Decabromodiphenyl ether, hexabromocyclododecane and antimony oxide have all been under toxicological and environmental scrutiny. A favorable risk assessment for decabro-

modiphenyl ether issued in Europe but is still under challenge. Risk assessments for hexabromocyclododecane and antimony oxide are underway at the time of writing this chapter.

SaFRon® 9010 and 9020 (ICL-IP) are water-dispersible proprietary solid blends of a bromine-rich flame retardant with an antimoldering additive, suitable for wash-durable flame retardant coating of cotton and polyester-cotton blends. A suitable aqueous dispersion uses 22 % SaFRon 9010 (which contains 55 % bromine), 3.6 % antimony oxide and 8.5 % acrylic binder. At 39.5 % total add-on, a cotton knit 200 g/m² fabric can pass the ASTM D6413-99 vertical test after 30 home launderings [86]. These blends are compatible with most textile finishing chemicals and show good pH stability. SaFRon® 9025 is a later addition to this series. It can be used on a wide variety of synthetic and natural fabrics, such as upholstery fabrics, and does not contain hexabromocyclododecane or decabromodiphenyl ether [87].

11.9 Coating with Bromine-Containing Emulsion Polymers

This approach is most suitable for 100 % polyester and for cotton/polyester blends. It uses a highly stable copolymer containing 35–45 % bromine (based on a brominated acrylate), which is available as a 40 % solid aqueous emulsion (TexFRon® from ICL-IP). The emulsion can be applied by padding, printing, knife-coating, kiss roll, or spraying. It can provide a flame retardant flexible film finish durable to 50 AATCC standard home launderings. For additional flame retardancy, it can be enhanced with antimony oxide. For backcoating, a thickener is usually added, and for improved durability, a crosslinker can also be used. Applications include apparel, bedding, awning liner, and work wear. A typical add-on would be 22 % total (17 % polymer, 7.3 % total Br) to pass CPSC CFR1615 after 50 home laundering cycles.

A transparent coating suitable for polyester and polyester/cotton blend is produced by applying a water dispersion of a copolymer of a brominated acrylate with an acrylic co-monomer with colloidal Sb₂O₅ as a synergist [88]. Because this coating is transparent it can be applied to the front and back sides of the fabric without an adverse effect on appearance.

These polymeric finishes can be viewed as having an environmental advantage over non-polymeric bromine flame retardants, since the polymers stay fixed in place and also are very safe from a toxicological point of view.

11.10 Backcoating of Carpets; Metal Hydroxide Fillers

It is common practice to pass carpet flammability requirements, such as the Federal “methenamine pill test” by use of alumina trihydrate (ATH) in the backcoating, bonded by a latex such as styrene-butadiene rubber. Ground calcium carbonate is often used as an inexpensive inert diluent. The use of low cost ground bauxite has been claimed in patents [89, 90] and has been shown in pilot trials to be practicable but gives the backing an off-white appearance. Inexpensive ground gypsum (a calcium sulfate hydrate with some flame retardant value) is sometimes used. The referenced patents are a helpful source on the formulation and application technology.

Metal hydroxides, in particular alumina trihydrate (ATH) and magnesium hydroxide, are widely used flame retardants in plastics but are effective only at high loadings, typically in the 60 % area, and have been useful in textiles only where a heavy coating can be applied as in backcoating of carpets. A thorough review, covering the metal hydroxides and related inorganic fillers as flame retardants from a basic standpoint, has been published by Hornsby [91].

11.11 Melt Processable Additives in Polypropylene

An detailed review in 2003 by Zhang and Horrocks [92] covers several decades of research efforts to flame retard polypropylene by melt additives or grafting which have led to little practical success.

Tris(tribromoneopentyl) phosphate (ICL-IP's FR-370®) at present is the most promising flame retardant additive which is usefully effective and thermally stable enough for melt spinning in polypropylene. It has the further advantage of being relatively light-stable especially when compared to aromatic bromine compounds. It can be used without antimony oxide which is an important advantage for textile fiber spinning since particulate solids can clog spinnerets and also weaken the fiber. Combinations of FR-370 with a small amount of a free radical generator such as 2,3-dimethyl-2,3-diphenylbutane (Akzo Nobel's Perkadox® 30 or Peroxid-Chemie's CCDFB-90) have been shown in a Bromine Compounds Ltd. patent [93] to have an activity advantage.

ICL-IP is offering a formulated additive system, SaFRon® 5371, a proprietary composition containing 63 % bromine and 2.6 % phosphorus, which is recommended for carpet fiber. This system avoids the use of antimony trioxide [94].

Grafting of pentabromobenzyl acrylate during melt processing of polypropylene has been suggested by Dead Sea Bromine (ICL-IP) researchers [95]. This method gives good launderability and color stability. It is not clear that commercial development has been successful.

Reportedly halogen-free flame retardant PP fibers were developed by Asota GmbH (Linz, Austria) [96]. In a carpet assembly they achieve the highest sl classification in the newly introduced European Radiant Panel Test prENISO 9239-1. The flame retardant additive used in the Asota fibers is not disclosed, but it could include Ciba's Flamestab® NOR 116. It is effective in PP fibers at very low level of 0.5–1.5 % for passing NFPA 701, MVSS 302 or DIN 4102/B2 standards [97]. NOR 116 is a thermally stable hindered amine (an oligomer-linked N-alkoxy-2,2,6,6-tetramethyl-4-substituted-piperidine which also provides improved UV stability to the fibers. PP textiles flame retarded with NOR 116 have better outdoor stability compared to FR-370. The mode of action may be, at least in part, the stimulation of melt flow.

11.12 Melt Processable Additives in Polyester Fibers

Various phosphate esters such as tetraphenyl resorcinol diphosphate have shown limited success as melt additives in PET. Exudation appears to be a shortcoming. A triphosphonate Rhodia's Antiblaze® (Amgard®) 1045 (related to the diphosphonate Antiblaze® 19 or Amgard

CU which is used in a thermosol method discussed above) has shown more promise [98]. Dispersing the liquid triphosphonate on a silica carrier aided dispersion in the polymer melt [99]. This additive was shown to be useful as a melt additive in PET, PTT and nylons used to make nonwoven fabric [100, 101].

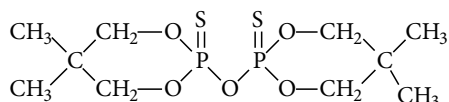
Apexical has introduced Pyrapex[®], a melt-processable additive for polyester fibers and nylons. It is disclosed to be an organic phosphinate (salt), high in % P, melting at 220 °C, and effective at low levels of addition. It is said to be particularly attractive as an additive for bicomponent nonwoven applications. The class of phosphinate salt flame retardants, generally available from Clariant, has recently been discussed in our review [102]. A Clariant patent application [103] suggests that zinc diethylphosphinate is particularly suitable for the fiber additive application because of its fusibility, and Pyrapex is likely to be this compound.

In a recent patent application to Wellman [104], a combination of phosphorus FR (preferred example not specified) with brominated FR (preferred example brominated polystyrene) and an antimony additive (preferred example sodium antimonate) allowed production of a polyester bedding filler passing the CAL 604 test based on weight loss over combustion for 6 minutes.

11.13 Inherently Flame Retardant Fibers

11.13.1 Rayon

The use of a phosphorus additive in viscose rayon was commercially developed by Sandoz and Lenzing AG [105]. It is now Clariant 5060. The compound used is a dithiophosphoric anhydride of the following structure:



Remarkably, this compound can be added to the highly alkaline cellulose xanthate “dope” before spinning. It survives the acidic coagulating bath and also survives alkaline laundering. This durability may be ascribed to “steric hindrance” by the branchy rings and to the deactivating effect of the sulfur atoms. It is believed to be in substantial commercial use by Lenzing.

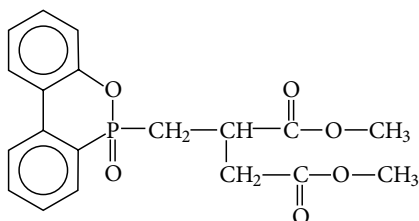
11.13.2 Polyester Fibers

At least two independent developments have become commercial. In Europe, a long R&D program at Hoechst [106] on the chemistry of methylphosphonous dichloride led to the development of a difunctional phosphinic acid or ester reactant, one useful form of which is the bis(hydroxyethyl) ester of $\text{CH}_3\text{P}(=\text{O})(\text{OH})\text{CH}_2\text{CH}_2\text{COOH}$. This can be reacted into poly(ethylene terephthalate) to give a flame retardant PET with less than 1 % P content needed to pass the typical vertical flame tests such as NFPA 701, by melt flow.

PET which incorporates this phosphinate built in is marketed at present by Invista; the fabric made from it under the name Avora®. This fabric not only has permanent flame retardancy but has good dimensional stability, wear properties and is colorfast. This fabric appears to have better wear properties than the topically treated flame retardant PET. It finds use in hotel and office furnishing, public transportation and industrial applications.

There has been some development, possibly to the commercial stage in China and Korea [107], of a P-phenyl analog of the above-described P-methyl intermediate. This was motivated by the broader availability of the intermediate $C_6H_5PCl_2$ compared to the less-broadly-available CH_3PCl_2 .

Toyobo (Japan) first developed an additive to be added in melt spinning of PET. This was a sulfonylbisphenol phenylphosphonate oligomer. It was commercially introduced as Heim® 1. Later, reportedly due to dye shade control problems, Toyobo switched to a reacted-in phosphinate of the following structure:



which was transesterified into the PET backbone [108]. Less than 1% phosphorus content suffices to flame-retard, probably by acid-catalyzed molecular cleavage favoring a melt-flow mode of extinguishment. The flame retardancy is retained through multiple launderings.

The sulfonylbisphenol phenylphosphonate oligomer additive, discontinued by Toyobo, is believed to be made and used in PET in China.

11.13.3 Polyamides; Aramids

Despite much effort, additive flame retardants and coreactant flame retardants seem not to have been successfully developed for aliphatic polyamide textile fibers, even though additives have been very successful for polyamide molding resins as reviewed by the present authors [109].

The successful flame retardant polyamides have been the aramids. The commercial examples are DuPont's Nomex® or DSM's Twaron® (poly-m-phenylenediamine isophthalamide), and DuPont's Kevlar® (poly-p-phenylenediamine terephthalamide). The aramid fibers have been reviewed by Gabara *et al.* [110].

Nomex® is used in fire fighters and military protective apparel and accessories, as well as electrical insulation paper. Hybrid knit fabrics of improved comfort and lower cost can be made by proprietary methods for layering Nomex with other fabrics, as in Alandale Knitting's strataTek® [111]. A special Nomex garment Limitedwear® garment was introduced by Du Pont in 2006 for military use, as coveralls for work involving flash fire hazard [112].

Nomex blended with Kevlar in fire fighters' outer protective garments is said by DuPont to have advantages of thermal performance, strength, comfort and durability including resistance to abrasion.

Kevlar, the most fire-resistant of the aramids, has been much used in military protective garments and protective fabrics in vehicles. Kevlar sewing thread is also useful in fire-resistant mattress construction.

11.13.4 Polyimide Fibers

Recent advances in high temperature melt spinning equipment have facilitated GE's recent introduction of low denier flame retardant fiber (Ultem® 9011) from their Ultem® polyetherimide and Extem® amorphous thermoplastic polyimide fibers, said to be useful for both woven and nonwoven applications, as well as in composite plastics. [113, 114].

11.13.5 Melamine Fibers

Basofil® is a melamine-based fiber from Basofil Fibers LLC, formerly a part of BASF. The chemistry, which appears to involve a cocondensation reaction of formaldehyde with melamine, substituted melamines and other formaldehyde-reactive compounds is shown in a series of patents [115, 116] and references therein. Besides the mattress application, Basofil is also useful in commercial aircraft seating, firefighter turnout gear, industrial protective clothing, friction parts, and automotive insulation.

A main feature of Basofil fiber for flame barrier applications is its ability to 'char-in-place' without shrinkage, when exposed to direct flame. Basofil fibers have an elliptical shape and very uniform diameter distribution (94 % within 10 and 20 μ). It is said that this denier distribution contributes to improved thermal insulative performance [117].

Blends of these melamine fibers with poly-m-phenylenediamine isophthalamide have been developed by Kermel (France) and Dystar® (Germany) for flame retardant military camouflage garments.

11.13.6 Glass Fabric

Woven fabric made from fine-diameter fiberglass is further coated with water-based polymers to make commercial products, Sandel® (Sancor UK, Ltd.) or VersaShield® TB 129 (Elk Technologies). These have been employed as a barrier fabric in furniture and military applications.

Various blends of glass fibers with aramids, melamine fibers, PVC fibers and polyester have been described for use in fire-protective non-woven veils for upholstery and mattresses [118].

11.13.7 Basalt Fibers

Basalt is a relatively low-melting natural aluminosilicate rock which can be spun into fibers, which can be used to make fabrics, barriers and insulation materials [119]. Fabrics made from

basalt yarn are obviously non-flammable but are difficult to sew, have poor seam strength and are easily damaged. A Belgian firm Masureel has overcome these problems with a treatment with a primer and silicone coating to produce Basaltex® Fire Blocker fabrics, suitable for interliner applications [120]. Basalt continuous fiber, roving and yarn are also available from AlbarrieCanada Ltd.

11.13.8 Silicic Acid-Containing Rayon Fibers (Visil®)

These inherently flame retardant viscose rayon fibers were developed in Finland by Säteri Fibers (formerly Kemira) and the technology appears to be disclosed in a patent by Parén and Vapaaoksa [121]. It is marketed by Ventex Inc. (Great Falls, VA) in the US and Canada. Visil is made by wet spinning of alkaline cellulose xanthate (viscose) containing a sodium silicate perhaps with some aluminosilicate component. During fiber coagulation, the silicate is converted to polysilicic acid, equivalent to about 30–33 % SiO_2 , which flame retards by both endothermic water release and char formation. A post-treatment by an aluminate salt may also be done. This fiber has been useful especially in blends. A brief review of Visil will be found in a chapter by Bajaj [5]. A related viscose rayon product, Daiwabo's Corona®, is made using sodium silicate in the viscose dope and then treating the spun fiber with a magnesium salt [122]. Related products are reportedly also made in China. The fibers find use in the US upholstery barrier fabric market and have been satisfactorily blended with modacrylics to improve overall flame resistance [2].

11.13.9 Halogen-Containing Fibers

The principal examples are the modacrylic fibers which are typically copolymers of vinyl chloride or vinylidene dichloride and acrylonitrile. Saran fibers (Dow and Asahi-Kasei), which are polymers of vinylidene dichloride, are commercially available, and are used mainly in upholstery for public conveyances, deck chairs, garden furniture and the like. Although these fibers do not melt-flow or drip, they shrink rapidly when exposed to the fire. Because of this, the best use of modacrylic fibers is in blends. Modacrylic fibers are briefly reviewed by Frushour and Knorr [123]. Blends of modacrylics with other fibers are discussed below.

11.13.10 Polyphenylene Sulfide Fibers

Recently, Diolen Industrial Fibers (Netherlands) introduced Diofort®, a high-tenacity multifilament yarn based on Fortron polyphenylene sulfide for use in woven fabrics, nonwovens, and as reinforcement. It provides flame, heat and chemical resistance, and toughness [124].

11.13.11 Oxidized Polyacrylonitrile Fibers (Pyron)

These black highly flame-resistant (char-forming) fibers made by oxidative degradation of polyacrylonitrile, such as Pyron® from Zoltek Corp., are low in resilience and compressibility and are said to be difficult to card and form into batts. Use of these fibers can be facilitated by blending with low melting binder fibers such as KoSa Type 254 Celbond® (a bicomponent

fiber with polyester core and copolyester sheath) and high melting carrier fibers such as KoSa Type 209 polyester. When subjected to fire, the polyester fibers rapidly retreat and leave a layer of Pyron® fibers to absorb and disperse the heat. Pyro-Gon® batts made in this way are suitable for protective workwear and mattresses (discussed below) [125].

Oxidized polyacrylonitrile fibers can also be made into a nonwoven surface “veil” where they provide a fire barrier but do not have to resist stresses [126].

11.14 Technology Related to Mattresses

11.14.1 Regulatory Actions Regarding Open-Flame Tests

The advent of open-flame tests, initially in California (Technical Bulletin 603, promulgated in 2005 for residential mattresses) and more recently on a US Federal basis by the Consumer Product Safety Commission (16 CFR 1633), in effect for mattresses manufactured or imported on or after July 1, 2007, has called into use various approaches to flame resistance. The requirements are similar to the California standard (peak heat release less than 200 kW during the 30 minute test), except that the Federal test allows only 15 MJ heat release in the first 10 minutes whereas California allowed 25 MJ. Testing and record keeping requirements are more severe in complying with the Federal standard. The Federal requirements, their justification and CPSC consideration of risks and benefits, have been published in a final rule document [127].

To pass this test, treating the mattress ticking is an infrequently-used approach. Merely preventing the ticking from burning is not adequate. Using a barrier (often a batting or nonwoven fabric) under the ticking is the predominant technical solution [128]. It was shown by Gallagher [129] that an interliner or backcoating must be carefully evaluated for each composite design since some interliners or backcoating combinations could actually increase heat release. It is also important that stitching of exposed seams including gusset, border and tape edge be done with flame resistant thread, such as Kevlar®.

As will be shown below, many alternative methods have been developed to pass the California and Federal requirements. The manufacturers have had to balance considerations of performance, cost, manufacturing flexibility, comfort and appearance. Some effort was expended during the period of standards development when leach resistance was thought to be necessary, but the final regulations have omitted that requirement. Some manufacturers choose to claim leach resistance as a positive feature even though not mandated.

11.14.2 Flame Retardant Facing

It is, of course, possible to avoid a separate barrier layer by use of a sufficiently flame resistant facing. Technology to accomplish this by attaching an intumescent foam layer to the bottom surface of the facing or to a fitted mattress cover is shown by Hairston *et al.* [130]. The disclosed intumescent materials include the typical ammonium polyphosphate, pentaerythritol and melamine combination, and in some instances a chlorinated paraffin oil, blended with a latex base.

Basofil Fibers offers a stitch-bonded nonwoven which can be used either as a flame barrier or printable flame-retardant ticking which requires no barrier and may have cost advantages [128].

11.14.3 Boric Acid on Cotton Batting

This inexpensive approach to a fire barrier is widely used to comply with the Federal open-flame mattress standard and could also be used in upholstered furniture [131]. According to claims by the manufacturer, such as Jones Fiber Products, the boric acid solid can be made to strongly adhere to the cotton (their T-Bond® method) so that it resists aqueous extraction and even vigorous jumping on the bed will not dislodge it. A patent application by US Borax [132] describes a means for increasing adhesion by including a small amount of an aminoalcohol or aminoacid in the boric acid formulation to form a glassy film.

11.14.4 Batting and Nonwoven Fabrics from Combinations of Flame Retardant Fibers

There have been many recent patents and patent applications on fiber combinations intended to meet the mattress standard. A representative selection will be presented and it is not always known to the authors which of these have been commercialized.

Nonwoven blends of a cellulosic fiber with at least 30 % of a modacrylic fiber, such as a Kanecaron® modacrylic fiber, (likely to be an acrylonitrile-vinylidene chloride copolymer possibly with added antimony oxide), advantageously “hydroentangled” with a second nonwoven layer of cellulosic, modacrylic and p-aramide fibers are claimed to pass the California mattress and bedding standard for open-flame test performance [133, 134].

Nonwoven interliners of specified loft, weight and density using a wide variety of flame-resistant fibers such as modacrylics (the now obsolete Courtauld’s Teklan® was preferred), wool or aramides are described in a 1992 patent application by Vita Fibers Ltd. [135].

DuPont has a patent application [136] on a high loft batting suitable for fire-blocking a mattress, comprising two layers of a flame resistant fiber such as Kevlar®, modacrylic or Visil-type rayon, each layer with specified composition, construction and thermal stability. Another DuPont patent application [137] discloses fiber barrier nonwoven fabrics composed of Kevlar® and Visil® rayon as single-layer fire blocking layers for mattresses. DuPont’s “Natural Fire Resistant High Loft” is a single-layer fabric or batting for mattress panels and borders using wool as one component and a silicic-acid-modified viscose rayon without topical treatment, optionally with an aramide [138].

Oxidized polyacrylonitrile fibers, such as Zoltek’s Pyron®, can be blended with p-aramid to make yarns with improved tensile strength and abrasion resistance. These yarns can be woven, knitted or assembled into felts [139]. Leggett & Platt is providing Pyro-Gon® batting as well as fabric for the bedding market.

A patent application by Small *et al.* [140] discloses mattress protection by a diverse series of nonwoven blends of non-fire-resistant fibers with flame retardant fibers and various flame-retardant-treated fibers (various specified semi-durable treatments such as intumescent phosphate or expandable graphite systems).

Modacrylic fibers such as those made by copolymerizing acrylonitrile with vinylidene chloride, may be blended with cotton or polyester fiber to make needle-punched nonwovens or knit fabrics suitable for mattress and upholstered furniture applications. Good flame retardant performance is achieved by the introduction of antimony trioxide into the spinning solution for the modacrylic fibers such as Kaneka's Kanecaron® [141].

Milliken inventors [142] show examples of blending flame retardant fibers such as oxidized polyacrylonitrile, Visil® rayon, or Visil plus Kanacaron modacrylic, with non-flame-retardant bulking fibers such as polyester and binding fibers such as low melting core-sheath fibers in a distribution gradient such that the majority of the flame retardant fibers are toward the outside of the resultant protective shield.

A barrier fabric which stretches and recovers particularly well to conform to a mattress substrate, is described by Link *et al.* in a patent to Freudenberg Nonwovens [143]. It combines any of a variety of flame retardant fibers with a dispersed, impregnated or intermingled elastomeric material such as Invista's Lycra® segmented polyurethane or DuPont's Neoprene®.

Another effective combination is a blend of melamine fiber (Basofil as discussed above) plus flame-retardant viscose fiber (Visil from Sateri Oy, Finland) plus modacrylic fiber and bonded with low-melting polyester fiber [144, 145]. The Basofil component provides good thermoinsulative properties and ability to char without shrinking, the Visil provides a siliceous matrix, and the modacrylic provides low local oxygen concentration to protect the char from oxidation. The low melting polyester provides a "carbon cement" to cohere the other fibers into a strong barrier.

Combinations of many of the above-described flame retardant fibers together with 25–40 % of a low melting binder such as low melting bicomponent fiber to make a protective batt for mattresses is described by Western Nonwovens inventors [146].

11.14.5 Corespun Yarn

One approach uses the patented McKinnon-Land's Alessandra® corespun technology wherein a blend of Basofil®, modacrylic and polyester fibers is wrapped around fine denier filament glass and nylon. The cost can be kept down by use of a majority of the lower cost polyester, while retaining good flame barrier action and good physical properties [144]. Other corespun flame retardant yarn technology is described by Land [147–151].

11.14.6 Mattress Construction

Serta, a leading US mattress manufacture, shows a double fire-resistant barrier construction, underneath the ticking, one barrier layer, then a cushioning layer, then another fire-barrier layer [152]. They mention use of Basofil melamine fabric (such as made from the Alessandra yarn mentioned above), Leggett & Platt's oxidized polyacrylonitrile fabric, or Jones Fiber's boric-acid-treated cotton batting.

Flame retardant nonwovens can be made which increase their thickness greatly and become effective barriers when exposed to fire, by compressing crimped heat resistant organic fibers onto an open-meshed scrim and holding them in a compressed state by a thermoplastic binder which can soften and release the compressed fibers when exposed to flame [153].

11.15 Future Trends

Upholstered furniture is being considered for a US Federal standard, but this has not yet been promulgated despite petitions to CPSC by the US fire marshals and despite statistics from the UK and the State of California [154] showing that the UK and California flammability regulations have been very successful in saving lives and property. The technical work for such a standard has been presented to CPSC, and California has already published a proposed open-flame test. As of the date of the present chapter, cover fabrics should pass a non-governmental Upholstered Furniture Action Council test for cigarette-initiated smoldering behavior which sets a limit on the loss of weight of a polyurethane foam substrate and allows no transition to visible flaming. Some of the present and pending standards may be met by foam flame retardants, others by the upholstery fabric, still others by barrier fabrics. The flame retarding of polyurethane foam has been reviewed by the present authors [155, 156] and is discussed in another chapter of this book.

Some unsolved problems exist with highly brushed cotton. Economics do not allow for a typical flame retardant finish. Efforts at Cotton Inc. are ongoing to solve this.

California open-flame standards (currently in development) for “top-of-the-bed” items such as pillows, comforters and mattress pads may call forth some new technology [157].

A large market is likely to develop in Asia, especially in China for flame retardant work clothing and furnishings for public buildings. The “center of gravity” for basic research on flame retardant systems appears to be shifting to Asia judging by the number of publications, and novel developments are likely to ensue from that source.

As in other segments of the flame retardant field, substitution of halogen and halogen-antimony systems, by phosphorus-based systems seems likely.

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12 Comments on Flammability and Smoke Tests

12.1 Introduction

This brief discussion of test methods is not intended to be exhaustive or authoritative, but only as an aid to the reader in identifying the test methods and standards we mention elsewhere in this book. For a broad overview of test methods used worldwide, we refer the reader to the Troitzsch monograph [1] and thorough reviews by Hirschler [2, 3]. An assessment of the fire-hazard-predicting value of the principal test methods, as applied to electrical and electronic materials, has been published by the leading Swedish fire research institute [4]. An overview of new and coming flammability regulations in the USA can be found in a 2008 paper by Hirschler [5]. Individual methods are usually available with detailed authoritative instructions from ASTM, UL and other organizations which promulgate methods and standards. The published test methods must be adhered to in detail if the results are to be claimed by the specified test, and it is not our intent to provide working directions in the present chapter. We will, however, discuss some practical modifications, problems, correlations, attempted correlations and extensions of the leading test methods.

Flammability of polymers is mainly assessed through ignitability, ease of extinguishment, rate of flame spread, rate of heat release, and smoke formation, distinguishable features of material response to fire. Depending on the application of the polymeric material, one or more of these flammability criteria should be measured by appropriate flammability and smoke tests. Numerous flammability and smoke tests are known and they are performed either on representative samples or on an assembled product. Tests can be small scale, intermediate scale or full scale. Although similar trends in the rating of materials can be found based on small and large scale tests, in general, there is no direct correlation between these tests. Improvements in flammability are sometimes accompanied by worse smoke generation. Once again, we remind the reader that small, medium and even large scale test methods assess only a particular fire risk scenario and cannot reliably predict performance in a real fire.

Some simple and inexpensive laboratory tests requiring only small samples have found broad utility. These tests are primarily used in industrial laboratories for screening materials and formulations for research and development, or for quality control. In academic laboratories, they have been suitable for studies of the effects of formulation ingredients or polymer structure on flammability. In this chapter we will shortly describe some commonly used laboratory test methods. We will also include some mention of pitfalls, modifications and precautions regarding these tests.

12.2 The UL 94 Vertical Flame Test

Underwriters Laboratories UL-94 Test (defined in ASTM D 3801, IEC 60695-11-10, IEC 60707 and ISO 1210) is designed for assessing “flammability of plastic materials for parts in devices and appliances”. It is run on a sample of the plastic itself, at specified dimensions, not on the finished part. This test measures how long a bar of polymer burns after exposure to a small gas burner flame, and it is a reasonable measure of a material’s response to a small ignition source such as a candle or a match. It is accepted for standardization in many countries and also internationally. Five different classifications from the vertical burn configuration are included in this test, but we will introduce here only V-0, V-1, V-2 classification, because it is most often cited in the flame retardant literature.

To assign this classification a plastic bar of 125 mm length \times 13 mm width, with smooth edges, is positioned vertically and held from the top. Depending on the application of the plastic, bars may have a thickness of 3.2, 1.6, or 0.8 mm. Thinner specimens are usually more flammable. A wad of surgical cotton is placed 300 mm below the specimen to detect flaming drips which will ignite the cotton. The Bunsen burner flame (ca. 19 mm high, fed with methane) is applied twice to the test bar (10 s each). After each application the burning time is recorded. The second application of the flame should follow immediately after the bar ceases to burn from the first application. A V-0 classification is given when the 5 test bars extinguish in less than 10 s after any flame application. The average burning time for 5 bars tested (10 flame applications) should not be greater than 5 s and there should be no burning drips that ignite the cotton. The individual specimen afterflame plus afterglow must not exceed 30 s. A V-1 classification is given to samples with maximum total combustion time < 50 s and average burning time for 5 specimens < 25 s. The individual specimen afterflame plus afterglow must not exceed 60 s. There should be no flaming drips. The sample is classified V-2 if it meets the flaming time criteria of V-1 or V-0 but has flaming drips that ignite the cotton.

Less flame retardant materials may be shown to extinguish after ignition in the horizontal position, usually designated as ASTM D635. An HB rating requires that the sample must either self-extinguish before a 25 mm reference mark or burn at a rate of less than 40 mm/minute for samples of 3–13 mm thickness, or less than 75 mm/minute for samples less than 3 mm thick.

A more stringent variant of the UL 94 test is often used to test office machine enclosures. The test bars are positioned as in the UL 94 test described above but the flame is applied five times (5 s each). To get a 5VA rating, no bar can have an afterflame time of over 60 s after the fifth flame application, and no drips are allowed that ignite the cotton below the sample. Another variant measures time to burn through the sample plate (5B criteria). Measurement of time to drip and time to burn through has been used as input data for statistical optimization [6]. Recently, Samsung researchers ran a comprehensive test with a set of styrenic resins flame retarded at HB, V-2, V-0 and 5V levels [7]. 19 inch computer monitors and 25 inch TV housings were molded from these resins and tested with various common household ignition sources like methenamine tablet, candle or paper ball. V-0 or 5V enclosures didn’t ignite, whereas HB and V-2 enclosures burned vigorously. Furthermore, a cone calorimeter study

showed significantly lower heat release rate for V-0 and 5V resins compared to V-2 and HB resins.

12.2.1 Precautions in the UL 94 Test

A careful study at Bayer Material Science [8] of variables affecting the reproducibility of the UL 94 test showed that for some materials, deviations for flame application as small as 0.5 s outside the protocol range and the flame pull-away speed can substantially affect the ratings. It was shown that scrupulous following of the UL 94 protocol is necessary.

Sources of scatter in the UL 94 and deviation from intrinsic flammability properties were discussed from an empirical and theoretical basis by Schreiber [9]. Bars which have built-in strain will sometimes distort in this test and should be annealed to allow strains to relax. Polymers containing polytetrafluoroethylene as a drip suppressant tend to shrink away from the flame. According to the UL 94 protocol, specimens which bend or shrink away should be followed manually with the burner. A further critique of the UL 94 test is included in a report from the leading Swedish fire research institute [4].

12.2.2 Variants of the UL 94 to Obtain More Quantitative Data

In a research study on a system with three flame retardant additives in EVA by one of the present authors, some statistical significance (reasonable correlation to compositional variables) has been found for the average burning times [10], although the truncated distribution caused by the “does not ignite” or “burns entire length” situations forces the experimenter to select only “on scale” results in order to get computable numbers. The experience of one of the present authors suggests that the burning times following the first ignition and the second ignition may each provide useful hints regarding exhaustion of a retardant (longer burning time after the second ignition) or build up of protective char (shorter burning time after the second ignition).

Researchers at GE [11, 12] have applied statistics to estimate the probability of passing UL 94 in the first try (first 5 bars). This appears to be a useful methodology when trying to go from a fairly reliable V-0 rating to a much more reliable V-0 rating. A useful application was the demonstration [13] that a very small amount of phosphoric acid (< 0.1%) added to a borderline-flame-retarded polycarbonate-sulfonate formulation, greatly improved the probability of a “first-time pass” in the UL 94 test.

The UL 94 test is also useful for observing melt flow, char barrier formation (amount, rate, texture, coherence, adherence), breaking of the barrier due to swelling, stretching or bending, open cell-closed cell character, edge burning, flickering, close spacing of burning times *vs.* widely divergent burning times, and afterglow. Careful observation of the burning phenomena and the burnt bar can often suggest causes of failure and means for improvement. Therefore, a compounder is well advised to carefully observe the UL 94 test in detail and not just accept the ratings done by someone else.

Tests resembling UL 94 but with longer burner exposures, measuring burning time and burning rate in both horizontal and vertical positions, have been used by the FAA to classify

aerospace materials [14]. The article discusses larger scale FAA tests using the Ohio State University rate-of-heat-release calorimeter.

12.3 Oxygen Index (Limiting Oxygen Index)

Another test commonly used in the R&D or control laboratory is the Limiting Oxygen Index test (LOI), also known as the Oxygen Index (OI). This method is included in some national or international standards, *e. g.*, ASTM D2863-97 or BS ISO 4589-2 or NES 714. The specimen size and shape is not as strictly specified as in the UL 94 test, but usually bars of about $100 \times 65 \times 3$ mm are used in testing of rigid plastics. The specimen is positioned in a candle-like fashion vertically at the axis of a glass chimney and clamped at the bottom. The chimney is continuously fed with a controlled mixture of nitrogen and oxygen. The flame of a small igniting burner is applied to the top of the specimen until the entire top surface is ignited. If the specimen does not ignite or extinguishes in less than 30 s, the concentration of oxygen is then increased, in steps with repeated trial ignitions, until the specimen shows stable candle-like combustion for more than 3 min after removal the ignition source or if more than 5 cm length of the sample is consumed, a new specimen should be put in place and tested at a slightly lower oxygen concentration. By iteration of these steps, finally the Limiting Oxygen Index value is determined; this is the highest concentration of oxygen at which the tested sample self-extinguishes in less than 3 min and less than 5 cm of the material is consumed. The LOI test does not represent any real fire scenario, but it is quite reproducible, and fairly insensitive to sample thickness. It is often used as a screening, research and statistical design tool, because it gives a numerical value typically to two (and with care and replication, three) significant figures, instead of a mere classification as given by the UL 94. It can even be run on films and textiles with suitable clamping.

Materials which melt and flow readily will often give high LOI values, and in the case of some such as nylon, it is even possible to arrive at two different LOI values depending on whether they are reached from the low oxygen side or the high oxygen side. If this contribution of melt flow is undesired, such as for a polymer which will often be used with a filler, a small amount of inert filler such as 1% fused silica or insertion of a glass thread will provide a wick and will retard the melt flow effect with a greatly depressing effect on the LOI. If the compounder expects that the plastic will be used with a filler, delustering agent, or inorganic pigment, then it is advisable to run the LOI with a component that retards the melt flow.

12.3.1 Oxygen Index – Correlation to Other Tests and Use in R&D

One of the present authors has coauthored reviews and statistical studies of the correlation of oxygen index to other test methods and to theoretical parameters [15, 16]. A weak correlation was found to peak rate of heat release by the cone calorimeter at the 25 kW/m^2 cone radiation level but no correlation at higher irradiation levels. This is explained by the oxygen index test having very poor coupling of heat from the flame to the surface of the polymer. In an incisive study, Lyon and Hughes [17] found that if peak rate of heat release is determined with a series of different radiation inputs, and the peak rate of heat release graphed against heat input from

the cone and then extrapolated down to zero heat input from the cone, the intercept on the heat release axis of the graph correlates quite well to the oxygen index. This is also not so surprising considering that the oxygen index configuration has quite low heat input to the sample.

Oxygen index shows useful correlations to char formation, heat of combustion (for materials which burn with little char), and to various practical tests such as the UL 94 and wire and cable tests, consequently the oxygen index continues to be used in both industrial and academic laboratories. Because it gives reproducible numbers to two and sometimes three significant figures, it is excellent for assessing synergism and antagonism of additives, and has often been accepted by patent examiners as evidence of unexpected positive deviations from additivity (“synergism”), a plausible basis for patentability of effective mixtures [18, 19].

Variations of the oxygen index methodology are often found in basic studies. As mentioned, the use of a glass fiber wick or a low percentage of an inert silica filler can often give results unconfounded by melt flow effects. Bottom-ignition LOI with a wick can be related to some fundamental burning properties and is discussed incisively by Stuetz *et al.* [20]. Thermal LOI, with a heated chimney, which is commercially available, can be useful especially for mechanism studies [21].

If instead of oxygen, nitrous oxide, a much weaker oxidant, is used, an indication about gas-phase or condensed-phase mode of action of flame retardants can be obtained [22]. For example, if a plot of oxygen index over concentration of the flame retardant is nearly parallel to the same plot for nitrous oxide index, mostly condensed phase action is postulated. On the other hand, if the oxygen index curve has steeper dependence than the nitrous oxide index over the concentration of flame retardant, contribution of gas phase action should be considered.

Additional information about flame retardant performance of polymers can be obtained from oxygen index test if oxygen concentration is plotted over time to extinction [20, 23] or over burning rate of specimens [24]. By extrapolation of these plots to zero burning time or zero rate, the lowest oxygen concentration at which polymer can be ignited is determined. The oxygen concentration at which combustion switches from self-extinguishing to self-sustaining mode can be also determined. The oxygen index device can also be used to measure *rate* of char formation, an often-overlooked but important parameter governing flame retardancy. This methodology is described by Zhu *et al.* [25, 26].

12.4 Glow Wire Test

This is more commonly used in Europe. It is defined in IEC 60695-2-10/13. The glow wire test (GWT) uses a heated hairpin-configuration resistance wire which is pressed, using a sliding rig, against the specimen for 30 seconds and then pulled back. The glow wire temperature is measured at which the specimen either ignites on contact or in 30 seconds after withdrawal and it is also noted whether burning droplets ignite a paper placed below the specimen. The glow wire ignition temperature (GWIT) is the wire temperature where the sample ignites with a flame of 5 seconds duration or more. The glow wire flammability index (GWFI) is

the temperature at which the flames burn for less than 30 seconds. These tests are in IEC 60695-2-10 to 13.

12.5 Hot Wire Index (UL 746C)

In this test, a specimen bar of specified dimensions is wrapped with five turns of resistance wire which deliver a reproducible heat load. Performance categories from 0 to 5 are defined on the basis of the time to ignition, from > 120 s to < 7 s.

A critique of hot wire and glow wire tests, in particular the observation that melt flow may give misleading results, is included in a report from the Swedish fire research institute [4].

12.6 Cone Calorimeter

The cone calorimeter test is a bench scale (medium size) test which was originally developed at NIST [27] and quickly gained popularity in the academic community as well as for standardization purposes (ASTM E 1354/ISO 5660-1, ASTM D 6113). It is also used as a tool for fire protection engineering, because it allows prediction of some large-scale test results, in particular flash-over time which is important for time to escape. In the cone calorimeter, heat and smoke release rate is measured together with mass loss and ignitability, under a wide range of radiant heat exposure conditions. At the start of a test, a square specimen of 100×100 mm is placed on a load cell and exposed to a preset incident heat flux from a truncated cone radiant heater, which can be set to fluxes representing small fires to fully developed fires. An electric spark ignition source is used for piloted ignition. The combustion products and entrained air are collected by a hood and extracted through a duct by a blower. Heat release rate is calculated from oxygen concentration measurements based on the oxygen consumption principle.

Apart from heat release rate, the cone calorimeter can also monitor time to ignition, weight loss of the sample during combustion, effective heat of combustion (heat generated per unit mass loss), rate of smoke generation, carbon monoxide, carbon dioxide and optionally some corrosive gases like HCl or HBr.

Some of the problems with the cone calorimeter are the following: the device is large and quite expensive, in the \$100K category, and requires careful calibration and recalibration. The burning is typically horizontal and may not appropriately represent vertical bottom-up burning. Samples that buckle, spall or intumesce can change the spacing to the heat source. In the extreme case, an intumescent material may actually expand into the heat source. Specimen restraints with such materials have not entirely solved the problem, as shown by Zhang *et al.* [28]. Practical findings dealing with sample thickness, sample retention and device maintenance from experience by himself and others in cone calorimetry were presented by Tu [29]. Suggestions for improving precision were the result of an interlaboratory comparison presented by Urbas in 2002 [30]. ASTM is addressing many of these issues and changes to ASTM standards based on the cone calorimeter are forthcoming at the time of writing this review.

12.6.1 Cone Calorimeter Correlation to UL 94

In a series of tests on 18 thermoplastics with UL 94 ratings from V-0 to HB [31], a very rough correlation was found with peak rate of heat release, average heat release rate and heat release at 60 seconds but no correlation at all with time to ignition or total heat release. Morgan [32] further explained inherent differences in the cone vs. UL 94 which make quantitative correlation difficult, but Lyon [17] showed that correlation is possible by using the peak rate of heat release axis intercept when a graph of the peak rate of heat release at various radiant heat inputs is extrapolated back to zero radiant heat input.

Another very broad empirical study by European investigators [33] of the interpretation of cone calorimeter results addresses the problem of applying this device to flame retardant screening. A critique of the cone calorimeter as applied to electrical and electronic material testing, and the relation of cone calorimetry data to other tests such as UL 94 as well as to real fires, is included in a report from the Swedish fire research institute [4].

12.6.2 Cone Calorimeter Correlation to the E 84 Tunnel Test (Discussed Below *per se*)

In a study by Janssens [34] using different kinds of wood products, a mathematical model (an exponential function) was developed for correlating flame spread index by the E 84 tunnel to ignitability and heat release rate as determined by the cone calorimeter.

In a study in which a small 2-ft. tunnel and several other fire tests were tried as predictors of the E 84 tunnel test, it was found by Ashland and Great Lakes Chemical researchers [35] that the best predictor for the E 84 test may possibly be the cone calorimeter peak rate of heat release.

A study at the US Forest Service laboratory [36] used the peak rate of heat release, total heat release and total smoke index to combine to a single fire growth acceleration parameter P , which showed a logarithmic relationship to E-84 flame spread index in the 25–75 range, and was able to discriminate between classes A, B and C.

Earlier work at Albemarle laboratories attempted to correlate flame spread index smoke index in E-84 with cone calorimeter data for flame retarded rigid PU foams [37]. They found that flame spread index has a good linear correlation with total heat released measured in cone calorimeter at 100 kW/m^2 heat flux. On the other hand, the smoke index better correlated with total smoke measured in the cone calorimeter at 40 kW/m^2 . These researchers also tested European foams rated in DIN 4102 B-1, B-2, B-3, and NFP 92-501 M-1, M-3, and M-4 (see below) and predicted that B-1, M-1 and M-3 foams most likely will pass the E-84 flame spread test.

12.6.3 Cone Calorimeter Correlation to Other Fire Tests

Cone data has been correlated to tests for wall coverings (ISO 9705, NFPA 265, and NFPA 286, construction product tests in the US (ASTM E 84) and building products in Europe (the Single Burning Item test, EN 13823). It can also be correlated with tests used for upholstered

furniture and mattresses in the US and Europe, and with a series of electrical cable tests in the US and Europe [38].

Carpenter *et al.* [39] have surveyed the relation of cone data to many reaction-to-fire tests and possible models correlating these in an ongoing program.

12.7 Steiner (25-Foot) Tunnel Test (ASTM E 84)

This test is used mainly for building materials in the US and is written into various building codes. The test apparatus is a tunnel measuring $8.7 \times 0.45 \times 0.31$ m ($25 \times 1 \frac{1}{2} \times 1$ ft) with viewing windows along its length. The sample to be tested is 7.6 m (24 ft) long and 0.51 m (1.67 ft) wide, mounted on the ceiling position (even if that is not how the product is to be used!). It is exposed for 10 minutes at one end of the tunnel to an 88-kW (5000 Btu/min) gas burner, with a forced draft through the tunnel, from the burner end, at an average initial air velocity of 1.2 m/s (240 ft/min). The flame spread index (FSI) is calculated on the basis of the area under the curve of flame tip location as a function of time, compared to assigned values of 0 for an inert board and 100 for a standard red oak flooring. The smoke developed index (SDI) is calculated from the area under curve of the light obscuration vs. time as measured at the tunnel outlet, and is, again, compared to the reference values of 0 for the inert board and 100 for the red oak.

With glass-reinforced thermoset laminates, it has been shown [40] that the reinforcement (glass) content and the thickness can have a significant effect on the flame spread and smoke evolved. Some codes require that the test be run on the minimum and maximum thickness and with construction similar to the manner in which the laminate will be used. The same researcher showed that the cone calorimeter data gave useful predictions of E 84 flame spread rating but not of the smoke rating.

12.8 NBS Smoke Chamber ASTM E 662

Although the cone calorimeter and the E 84 tunnel give smoke readings, many commercial standards for smoke are written to the NBS smoke chamber, in which small vertical samples are burned under both smoldering and flaming conditions, and the smoke accumulated (unlike the cone or the tunnel where readings are continuous) during the burn for measurement photometrically. A critical overview of the NBS smoke chamber was published by British workers [41] who suggest improvements in the methodology to get more consistent results.

12.9 Federal Apparel Test (16 CFR Part 1610)

The conditioned fabric sample is held at a 45° angle in a specified frame and ignited for a short specified time by a needle flame. The flame spread rate is measured. The flame must not reach a mark in less than 3.5 seconds (or 4 seconds if a raised fiber fabric). This is a very lenient test, passed by almost all apparel fabrics except for some “high loft” cotton fabrics.

12.10 Federal Children's Sleepwear Test (CFR Title 16, Parts 1615 and 1616)

The conditioned fabric is held in a vertical position in a specified manner and exposed at the bottom by a standard burner flame for 3 seconds. The fabric must extinguish and the distance burned must not exceed an average of 7". The original test had a flaming drip prohibition but the test was later modified (after toxicity problems with tris(dibromopropyl) phosphate, one of the main flame retardants used on polyester fabric to pass this test) to remove this requirement. Consequently, many non-flame-retarded thermoplastics such as polyester and nylon can pass by melting and dripping. Cotton and cellulosic blends can only pass with a suitable finish.

12.11 Textile Test NFPA 701

This is a test requirement for fabrics used, for example, in public occupancy draperies. Its vertical configuration and bottom ignition by a gas burner resembles the sleepwear test but the average weight loss is measured, which should be less than 40 % for 10 specimens. The fragments that fall to the floor of the test chamber should not burn more than an average of 2 seconds.

12.12 Textile Test ASTM D 6413

This is rather similar to the two tests above. It is also Method 5903.1 of Federal Test Standard 191A. A 12" specimen of fabric is suspended vertically in a specified clamp and a controlled burner flame is applied to the bottom edge for 12 seconds. Afterflame time, afterglow time and char length is measured. This test is typically used for protective garments. NFPA specifies maximum of 2 seconds afterflame. Several organizations specify maximum char length of 4 or 6 inches.

12.12.1 Test Specific to Upholstered Furniture: Cigarette Ignition

In the US, there is a voluntary Upholstered Furniture Action Council (UFAC) cigarette ignition test, accompanied by a hang tag with warnings. This has evidently helped guide design and construction to less cigarette-ignitable materials.

12.12.2 Tests Specific to Upholstered Furniture: California Technical Bulletin 117

The state of California California Technical Bulletin 117 is a mandatory standard, with both an open flame test and a smoldering cigarette test for the component materials used to make residential upholstered furniture. In this test, each upholstery component except the covering fabric is time exposed to either an open burner flame or a smoldering cigarette in a defined test chamber. In the open flame test, the flame staying on the sample or the afterflame of any drips cannot exceed an average of 5 seconds, and any one specimen cannot exceed 10 seconds.

The char length cannot exceed average of 6 inches and any one specimen cannot exceed 8 inches. In the cigarette test, the char length is measured to a specific specification criteria contained in Technical Bulletin 117 and the foam sample must retain 80 % of its original weight after the cigarette has completely burned and the char scraped off the foam.

12.12.3 Tests Specific to Upholstered Furniture: California Technical Bulletin 133

California Technical Bulletin 133 is a very severe open-flame test, mandatory for furniture sold for public occupancies. A full scale piece of furniture or a mock up is exposed to a 16 kW open flame for eighty seconds. The temperature at the 4 foot level and at the ceiling, the mass loss, smoke and carbon monoxide are measured and must not exceed stated criteria. The cone calorimeter can also be used, and there are allowable limits on peak heat release and total heat release. There are specific criteria for peak heat release and total heat release.

As of the time of our present review, the US Consumer Product Safety Commission has not issued proposed standards for open-flame testing of upholstered furniture, although they have devoted extensive laboratory effort to developing such a test.

12.12.4 Tests Specific to Upholstered Furniture: British standard

The UK, having experienced severe fire incidents with upholstered furniture, particularly with polyurethane foam cushions, instituted a fire standards and test requirements for all upholstered furniture. A principal standard is BS 5852 with various size open-flame ignition sources using wooden block assemblies, (a “source 5” crib is most severe). The standard also addresses cigarette ignition, applied to a mock-up of the upholstered seating. Statistics support the efficacy of the British standards in reducing upholstered furniture related fires and casualties.

12.13 Federal Motor Vehicle Safety Standard 302

This Federal test, equivalent to ISO 3795 and SAE J369, is required for materials used in the passenger compartment of an automotive vehicle. A 4" × 14" sample of the material at its proposed use thickness (not to exceed ½") is clamped in a horizontal position and ignited by a standard burner flame. The rate of burn must not exceed 4"/minute. This is a rather lenient requirement and some manufacturers specify a slower burn.

12.14 French Epiradiateur Test (NF P 92-501) for Building Materials

The specimen is ignited at a 45° angle under irradiation by a standard electrical heater. The ignition time, flame heights, and total combustion time are measured and combined in a formula to compute a classification index from M1 (best) to M4 (poorest). This device can be used to meet French standards NF P 93-507 and others.

12.15 Carpet Tests: Pill Test and Radiant Panel

Residential carpet must pass the “pill test” (ASTM D 2859-96, 16 CFR Part 1630.4, 1631.4). A combustible methenamine pill is ignited on the sample in the middle of a circular steel frame. The charred area must not reach to 25 mm from the frame in 7 out of 8 specimens. Most thermoplastic carpets pass easily; cotton shags generally fail.

A much more demanding carpet radiant panel test (ASTM E 648-99) is usually required for commercial and public buildings. The specimen is ignited under a standard radiant heat flux profile and the distance traveled by the flame front is measured and converted to the critical heat flux required for ignition.

12.16 Roofing: the Burning Brand Test

This test, ASTM E 108-00 (UL 790, NFPA 256), is run with the roofing sample at an adjustable angle. Ignition may be by a gas burner or a specified burning wood brand. Flaming should spread less than 6 ft. for a class A roof (affording a high degree of fire protection to the roof deck).

12.17 Large Scale Tests

The reader is referred to Troitzsch [1] and Hirschler [2, 3] for an overview.

An important but expensive test used in the US is the room-corner test (Factory Mutual 4880) for building materials. This test requires a special large instrumented burn room with non-combustible walls. The sample, usually a 25 sq. ft. piece, is placed vertically for wall materials or horizontally for ceiling/roof materials, and ignited by a large wood pallet placed in the corner with the sample. The fire must not be self-propagating enough to reach any structural limits. Heat measurements are usually made to permit a flame spread parameter to be calculated.

In Europe, a consensus test is the single burning item (SBI) test (EN 13823), which is the basis for the reaction-to-fire classification system for construction products in the European Union. In this test, two specimens (such as wall or ceiling finish or insulation), both 1.5 m high and one 0.5 m wide, the other 1 m wide, are placed in a corner of the test chamber and exposed to a 30 kW propane burner. Ignitability, flame spread, heat release, smoke and flaming droplets are measured, to compute fire growth rate (FIGRA) and smoke growth rate (SMOGRA). It might be noted that, since these are rate measurements, a material which gets to high heat or smoke quickly may rate more poorly than one which takes a long time to release even more heat and smoke.

A recent Swedish study [42] shows useful correlations of FIGRA (by SBI test) to cone calorimetry, to the room-corner test, and suitable for predicting flash-over time. In the Euroclass performance-based system, different testing systems can be related to each other. A brief critique of the SBI test, as applied to electrical products, is included in a report from the Swedish fire research institute [4]. It was also pointed out that metal-covered sandwich panels which get a favorable rating in the SBI test can fail the room corner test [43].

12.18 Other Specialized Tests

Upholstered furniture or mattress tests ASTM E 1537/CA TB 133/ASTM E 1590/CA TB 129/CA TB 603/16 CFR 1633/CBUF are discussed in the chapters on textiles and polyurethanes. The recently promulgated Federal mattress standard which requires a large open flame ignition source is important, and technology to meet it is discussed in our Textile chapter. Issues associated with and benefits of the Federal 16 CFR 1633 standard from the point of view of the mattress industry are summarized in a 2007 paper by Trainer [44]. This test as well as TB 603 and TB 604 were reviewed by McFadyen from the prospective of the FR fiber manufacturer [45].

Wire and cable tests (UL 1581-1160/UL 1685/ASTM D 5424/ASTM D 5537/IEEE 1202/CSA FT 4FIPEC, IEC 60332-3) are a complex subject. Reference should be made to Troitzsch [1] and Hirschler [2, 3]. Cables for different applications have different requirements, many of the tests involve large cable tray configurations, and the latest National Electrical Code should be consulted. Recently, a European fire regulators group and the European Council drafted fire safety requirements for all cables installed in buildings [46]. Researchers and compound developers on this topic often make use of small tests such as oxygen index, UL 94, the NBS smoke chamber, and the cone calorimeter in arriving at improved formulations worth the expensive full scale testing.

12.19 Warning Regarding Interpretation of Fire Tests

To end our this chapter and our book with the same warning as we gave at the beginning, we want to emphasize that most claims that a given product acts as a flame retardant or is flame retarded are based on small or medium scale tests, which do not necessarily predict behavior in a real fire. Indeed, most retardant systems can be defeated by a large-enough fire. The fire performance of a product can be profoundly affected by fillers, coatings, laminates, pigments, dyes, delustering agents, plasticizers, crosslinking agents, processing aids and other compounding ingredients, and also by the physical factors of shape, thickness, presence of apertures, position, ventilation, temperature and proximity to other materials. The fire performance can of course also be affected by the size and temperature of the igniting flame or other heat source, and by the time period available for ignition to take place. Fire propagation, smoke and carbon monoxide yield is greatly influenced by ventilation. In view of the many “real world” variables, the authors cannot warrant the performance of any mentioned flame retardant system, and we cannot advocate any particular choice of retardant. The users of flame retardants not only must comply with fire and smoke standards, but must also bear the responsibility for the fire performance of their products under anticipated realistic use conditions.

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13 Overview of Modes of Action and Interaction of Flame Retardants

13.1 Introduction

We present a very abbreviated discussion here and refer the reader to more detailed reviews published elsewhere [1–3]. We believe that it is helpful for the compounder to have some understanding of the mode of action of the various flame retardants, so as to facilitate the best choices to meet required standards, to make use of the many favorable combinations possible, and to be cautious about conflicting combinations.

In the broadest sense, the retardants may work by a physical or chemical mode, or both modes together. They may also work in the flame or in the condensed phase (solid or molten polymer phase), or in both. In the physical mode, they may be simply “heat sinks”, fuel diluents, or barrier-formers. In the chemical mode, they may affect the manner in which the polymer breaks down or they may effect the propagation of the flame.

We will not attempt to get into the molecular chemistry more properly known as “mechanism”. In fact, the details are, in most cases, not known, poorly understood, or controversial, since the fire process is complicated in time and space, and experimental methods are fraught with difficulty. Polymer degradation, especially in the charring phase, is poorly understood. Flame chemistry and physics are surprisingly complex and the interested reader is referred to a monograph on this topic [4].

13.2 Heat Sinks (Heat Capacity Effects and Endotherms)

Additives such as clays, talc, silica or magnesia may simply represent non-combustible material which has to be heated up in order to bring the combustible part of the mass to ignition temperature. This mode of action generally requires very high loadings and is most satisfactory in elastomers which can tolerate such loadings without losing useful mechanical properties. It is mainly of value in combination with other flame retardants.

A more potent “heat sink” mode is that of additives which decompose with uptake of substantial heat (endothermic decomposition), and which do not release flammable vapors on doing so. Leading flame retardant additives with this property are aluminum hydroxide (alumina trihydrate, ATH, which begins to release water around 200 °C), magnesium dihydroxide (MDH, which releases water at about 300 °C), basic magnesium calcium hydrate carbonate, (hydromagnesite), huntite-hydromagnesite, hydrated zinc borates, and to some extent, uncalcined clays. Calcium carbonate is somewhat too stable to be effective in this mode except in some formulations where it can provide a high temperature endothermic action.

Not only is the water release endothermic, but also the water thus released takes up heat radiated from the flame on its way into the flame zone. In addition, it dilutes whatever fuel

is also released from the pyrolysis of the polymer. Moreover, the residual solids after their water release has occurred still provide heat- and mass-transfer barriers. All of these modes must occur; data is scarce or non-existent to show their relative importance.

Besides heat sinks which are water-releasing and fuel-diluting, some other cases are of importance. Melamine is used as a flame retardant component, sometimes by itself as in polyurethane elastomers, but more often in combinations with other flame retardants such as with chloroalkyl phosphates in flexible polyurethane foams [5]. Part of its mode of action must be endothermic evaporation, endothermic dissociation (see below), and dilution of the fuel with a low-combustibility vapor.

13.3 Heat Sinks in the Vapor Phase

This is one of the least understood areas of mode of action, and indeed often overlooked despite the possibility of its great importance. Studies done with flame extinguishants (not in polymer systems) show a remarkable quantitative relation between flame inhibiting action and computed endothermic dissociation enthalpy and heat capacity [6]. In a study more related to polymers, the heat capacity effect of hydrogen bromide and hydrogen chloride was shown to be a main (although probably not exclusive) contributor to their mode of action [7, 8]. This may be a more important part of the action of hydrogen chloride, and a lesser part of the action of hydrogen bromide. In both cases, fuel dilution by these non-combustible gases is important, as is the effect of an outflowing stream of non-combustible gas causing whatever fuel is also in the stream to be propelled past the flame zone before the fuel is fully oxidized.

A further mode of physical action of melamine (see prior section) is the reported dissociation of the intact melamine molecule in the vapor phase to form cyanamide, which may further dissociate endothermically to nitrogen-rich poor fuels [9].

Chlorine-rich polymers such as PVC [10] or PVDC, as well as chloroparaffins [11], also dissociate endothermically with release of HCl, a non-fuel.

Some evidence was adduced that tris(dichloroisopropyl) phosphate, a widely used flame retardant in flexible polyurethane foam, may be working largely in a physical mode (at least in the upward burning configuration), by evaporating as the intact molecule prior to evolution of fuel (diisocyanate) from breakdown of the foam [12]. This phosphate is a poor fuel or even a non-fuel and its outward flow of vapor from the heated foam prevents ignition of the foam as well as cooling the surface of the foam. This may not be the only mode of action; in downward-burning tests there is evidence of a surface barrier effect.

13.4 Barrier Effects

A gaseous “blanket” of non-combustible gases over the surface of the fire-exposed polymer, excluding oxygen from the surface, is often hypothesized as a flame retardant mechanism, particularly for halogen or halogen-antimony systems. The importance of excluding oxygen from the surface is surprisingly an unsettled question. In some fire configurations, the surface

is extremely oxygen-depleted, and fire modeling is often done using a simplifying (oversimplifying?) assumption that the pyrolysis of the polymer is anaerobic and that all the oxidation takes place in the flame zone. Some compelling evidence that this is not true was published by Celanese researchers who showed major surface and subsurface oxidation in the case of polypropylene [13, 14]. This could be an important mechanism where there is access of air to the burning surface, as in the important situation of upward burning where air is probably convected into the zone between the flame and the heated surface. Surface oxidation is often neglected in theoretical modeling but needs more experimental investigation.

Another physical mode of action, often resulting from a chemical mode of action such as char formation, is formation on the surface of a fire-exposed polymer of a barrier to heat transfer and mass transfer. Charrable polymers will generally form such a barrier, especially if induced to do so by a char-inducing catalyst. This is a main mode of action of many phosphorus-containing flame retardants when they are used in polymers that have char-forming characteristics, mainly those polymers which have oxygen or nitrogen in their structure. The char-forming action is also often endothermic (at least in its earlier stages) and water-releasing, providing further contributions to flame extinguishment.

A char barrier must be reasonably coherent and continuous. If it has too many holes or cracks, it can be ineffectual [15]. It is believed that so-called "turbostratic" char which is composed of amorphous phase of carbon black and various precursors of the char with randomly distributed islands of graphitized carbon is the most efficient as a protective layer, because the amorphous part usually molten at the high temperature helps keeping flexibility and fluidity of the char, whereas graphite regions provide reinforcement and protect against oxidation (burn out, glowing) [16]. Little or no flame retardancy results from dispersing powdered charcoal or carbon black in a polymer. If the char is made to form in a poorly-charring polymer by adding a powdered char-forming additive, it is important that the char be coherent, not particulate. It seems important that if a char-forming powder is added to a poorly-charrable polymer in order to form a char barrier, the char-forming additive should melt and flux together prior to charring.

An exception to the futility of adding powdered carbon is the great benefit of adding expandable graphite (acid-treated graphite). Although it is ineffectual as a fine powder, granular expandable graphite is very effective. It expands about 100 times its original volume and forms a thick mat of tangled twisted graphite fibers, and although this is not a continuous film, the expanded graphite layer is thick enough and formed rapidly enough to provide a heat-transfer barrier which is very effective in flame retardancy [17]. Expandable graphite can be used where a coarse black electrically-conductive filler is acceptable.

Another postulate that is often made for the mode of action of non-volatile phosphorus flame retardants is that they coat the surface of the burning polymer with phosphoric or polyphosphoric acid [18]. This is qualitatively observable, for instance by infrared or even by washing off and titrating the acid. It is surely an important part of the afterglow inhibition action of phosphorus flame retardants. The coating effect is suspected of being quite important, and may be involved in some of the strong effects of phosphorus synergism by some nitrogen compounds [19] or metal salts [20], but quantitative studies of this mode of action are lacking. Coating with phosphoric acid is probably quite important in intumescent systems, where typical additives such as ammonium polyphosphate can generate polyphosphoric acid, which

must coat the char. There, it may serve as a barrier to the diffusion of oxygen to the polymer or char surface, or to some extent as a barrier of diffusion of the fuel to the flame. It is also known that phosphorus compounds can deactivate especially oxidizable sites on carbon.

Another significant family of barrier materials is siliceous materials. The addition of silica by itself is ineffectual because it is too high melting. Small amounts of silica can aid or oppose other flame retardant actions by exerting melt-flow and wick effects. Silicic acid (hydrated silica) is effective to a commercial degree in viscose rayon (Visil®). Work at NIST also showed that silica gel provides flame retardant action through modification of polymer melt viscosity and building siliceous barrier [21]. Very low melting alkali metal silicates are generally water-soluble but are suitable for non-durable (disposable) flame retardant applications such as paper. Some moderately low melting borate-silicate glasses, available as powders (frits) seem to be useful contributors to the overall flame retardant effect of a multi-component formulation.

Organic silicon-containing products, such as some silicones, are useful, generally not as free-standing flame retardants but as adjuvants. For example, phenyl methyl siloxanes appear to be useful flame retardant components in epoxy-based printed wiring boards, where another main contributor to the flame retardancy is based on a particular type of char-forming epoxy (see Epoxy chapter). Phenyl methyl siloxanes are also useful in polycarbonates where they seem to have two modes of action:

- (1) in the molten polymer they migrate quickly to the surface and
- (2) they form siloxane cross-links which prevent dripping [22].

Some oligomeric methylsiloxanes are useful as flame retardant adjuvants, for example, Dow Corning DC-4071. It is more likely that they do not form a continuous siliceous barrier but may work more by forming a radiant-heat-reflective layer on burning plastics.

Low melting glasses, and especially devitrifying glasses which form a ceramic layer when strongly heated, also have been often proposed as barrier components, although commercial examples are few. Zinc alkali phosphate glasses from Dow Corning are examples of such glasses [23].

Borates also can be barrier formers. Particularly in combination with ATH, $\text{Mg}(\text{OH})_2$ or other solid mineral additives, zinc borates can form a sintered mass which acts as a fire barrier [24]. Boric acid in cotton batting fluxes when exposed to flame, releases water, provides an endotherm, and forms a protective glass. Sodium borate (borax) has a long history of flame retarding cellulose (wood, textiles, paper) and a substantial part of its action is attributed to formation of a glassy coating, which may be foamed due to the release of water vapor.

Layered clays, such as montmorillonite, can be made to separate into individual leaflets of about 1 nanometer thickness and orders-of-magnitude greater length and breadth. These are usually called “nanoclays”. The separation into leaflets (exfoliation or delamination) is accomplished by introducing compounds or polymers which spread and cause the release of the leaflets. In a burning polymer, these nanoclays form surface barriers as the polymer burns away, and contribute to flame retardancy or at least to reduced rate of heat release [25]. The nanoclays have not been found to be “stand alone” flame retardants but usually contribute to

flame retardancy in combination with other retardants. In char-forming systems (see below), they often form good char-clay barriers on the burning polymer.

It is worth noting that barrier formation mechanisms, such as surface char formation, have an advantage over flame inhibition mechanisms because they do not cause an increase in smoke, carbon monoxide and corrosive gases.

13.5 Flame Inhibition Effects

Flames are complex series of oxidation reactions [3], but the rate controlling step is a branching step, where atmospheric oxygen (O_2) reacts with hydrogen atom $H\cdot$ (derived from the fuel) to form O atom (a very reactive species) and hydroxyl radical ($OH\cdot$; also a very reactive species). The O atom can attack a hydrogen molecule or a C—H structure to make OH radical and a H atom or carbon radical, a further branching step. Thus, one high-energy species yields two high energy species, a branching step which is critical to flame propagation. The main heat-producing step in a typical flame is $OH\cdot$ attacking CO to form CO_2 and H atom.

Of course, preventing access of oxygen (such as by a barrier or outgoing stream of gas) will prevent that step, but in most ventilated flames, oxygen is sufficiently available. The scarcer (rate-limiting) species, $H\cdot$, can be scavenged in either of two ways. One important way is that $H\cdot$ can be made to react with some component (such as HBr) to give the less reactive H_2 and the relatively less reactive $Br\cdot$ [26]. The hydrogen atom $H\cdot$ can also react with volatile antimony tribromide or trichloride to form HBr or HCl and the relatively less reactive $SbBr_2\cdot$ or $SbCl_2\cdot$ which can further undergo reactions with $H\cdot$ to give SbBr and SbCl and ultimately Sb.

Another way to scavenge the hydrogen atoms ($H\cdot$) to quench the flame is to cause them to recombine to form relatively unreactive molecular hydrogen (H_2). It is a physical law that two fast-moving bodies, such as atoms, cannot recombine unless the momentum can be carried away, generally by a third body. This requires third body collisions which are infrequent, unless there is a surface present. Finely divided solids, such as smoke particles or a vapor-phase finely-divided solid antimony species, or the white smoke from sublimed melamine, may serve as hydrogen atom recombination sites.

Many solid powders can also quench flames efficiently; this mode of flame extinguishment being used in solid fire extinguishers. Recombination sites may play a part in this mode of action but endothermic volatilization of the solid is probably more important. It is possible that part of the action of melamine (which forms a white smoke) is of this type.

Besides the halogens and antimony, there are other powerful vapor phase flame inhibitors. A broad comparison was done at NIST using measurement of the inhibition of premixed fuel-air flames [27]. Interestingly, various phosphorus species were at the most active end of the scale, the halogens being roughly in the middle. Some relatively volatile phosphorus compounds are believed to exert their activity to a large degree in vapor phase flame inhibition; examples being dimethyl methylphosphonate (which is used in thermoset resins), and triphenyl phosphate, probably lower-alkyl-substituted phenyl phosphates, and to some degree, tetraphenyl resorcinol diphosphate in styrenic plastics. The mode of action may be analogous to that of HBr, namely phosphorus species, perhaps small fragments such as PO_2 and HPO_2 , may scavenge hydrogen atoms and act as flame inhibitors [1, 2, 28].

A method was proposed for distinguishing condensed phase modes of action from flame inhibition, namely determining the effect of the flame retardant at varying concentrations when the sample is burned under N_2 - O_2 atmosphere and under N_2 - N_2O atmosphere. If changing the oxidant has little or no effect on retardant efficiency, the retardant must be acting in the condensed phase and not in the flame [29]. Such a comparison in rigid polyurethane foams (using this oxygen index vs. nitrous oxide index means for distinguishing vapor phase from condensed phase activity) showed that trimethylphosphine oxide (volatile but stable) was mainly vapor phase, dimethyl methylphosphonate (volatile but less stable) was part vapor-phase, part condensed phase and triethyl phosphate (which cracks to non-volatile ethyl acid phosphates) was mostly condensed phase mode-of-action [30].

13.6 Char Formation

Polymers which form a high yield of carbonaceous char when strongly heated under air tend to be inherently flame retardant, examples being polyimides, polyaramides, liquid crystal polyesters, polyphenylene sulfide, polyarylenes, and many thermosets. In fact, it has long been known that the oxygen index correlates quite well to char yield for the higher charring polymers. One reason is that char represents carbonaceous material that didn't burn, thus the actual heat of combustion is lowered by the theoretical heat of combustion of the char. A second reason is that char represents a barrier to protect the underlying material. Moreover, the formation of char in the case of oxygen containing polymers is often accompanied by the release of water, or in the case of polycarbonates, the release of carbon dioxide.

Curiously, although the *yield* of char in relation to flame retardancy has been well studied, the *rate* of charring in relation to flame retardancy has not been much studied, although some studies indicate its likely importance [31, 32].

A substantial class of important polymers, such as polyesters and polyamides, containing oxygen and/or nitrogen, char poorly in the pure form but can be induced to char by appropriate additives, most commonly, acid-generating additives. Additives that generate volatile acids such as hydrochloric are not especially effective because the acid is immediately volatilized. Less volatile is sulfuric acid but it too is partially lost by volatilization. Sulfuric acid and its thermally decomposed derivatives such as ammonium sulfate or ammonium sulfamate are effective in polymers that char rapidly, such as cellulose, but are lost too soon in slow-charring polymers. The ideal acid for catalyzing char in a burning oxygen- or nitrogen-containing polymers are phosphoric acids or polyphosphoric acids, which are substantially non-volatile. Since the acids are usually not suitable as polymer additives, thermally decomposable salts and esters of phosphorus acids are used. These represent one of the leading classes of flame retardants, used in a wide variety of charrable polymers. Further on, we will discuss how these same phosphorus compounds can be used in non-charrable or poorly-charrable polymers. The leading char-inducing phosphorus compounds are ammonium phosphates (water soluble), ammonium polyphosphates (both water soluble and insoluble types), melamine phosphate, melamine pyrophosphate, melamine polyphosphate, ethylenediamine phosphate, piperazine pyrophosphate (insoluble polymer), and a wide variety of phosphate and phosphonate esters, which are discussed in other chapters.

Polymers which char on heating often crosslink prior to char formation, and, moreover, crosslinking between polymer chains is generally an important step during char formation. However, the opposite is not always true; polymers which are crosslinked (thermosets) or cross-link during decomposition do not always give extensive char. Charring usually depends on the type of crosslinks, *e.g.* crosslinks containing aromatic groups are always beneficial for charring, whereas aliphatic crosslinks may decompose as easily as non-crosslinked polymer [33]. Crosslinking, prior to and during char formation, generally reduces the rate and amount of volatile fuel and thus starves the flame. The flame retardants, such as phosphorus compounds, which increase char formation generally lower the decomposition temperature of the polymer somewhat.

In the case of polyvinyl chloride, which loses its chlorine content as hydrogen chloride when exposed to fire, it is commercially useful to retard smoke formation by introducing solid catalysts, typically Zn, Sn and/or Mo-based, which favor char formation (*via* dehydrochlorination) and lessen cracking to aromatic fragments which tend to form soot [34]. Zinc borates, zinc stannates and ammonium or melamine molybdates are often used for this purpose.

13.7 Char Formation in Poorly Charrable Polymers

The polyolefins, diene elastomers, and styrenic polymers, or briefly stated, polymers with little or no oxygen or nitrogen content, tend to pyrolyze to fuel gases, and give little or no char when exposed by themselves to flames. To make use of the char-formation mode of flame extinguishment, it is necessary to add an effective and preferably compatible char-forming ingredient, along with a flame retardant of the type that induces char, such as a phosphorus compound. A very successful example of this principle is Noryl®, a blend of impact polystyrene (poorly charrable) with poly(2,6-dimethylphenylene) oxide, “PPO” or “PPE”(ether), a good char former. Another successful example is the blend of ABS (a poor char former) with bisphenol A polycarbonate (a good char former). In each of these two cases, incorporation of an aryl phosphate to provide catalysis of char formation provides the blends with adequate flame retardancy.

Even small amounts, in the 5–10 % range, of the good char-forming polymer such as PPO, along with a good char-forming catalyst, such as a phosphate, can afford adequate flame retardancy in some cases.

13.8 Intumescence and Formation of a Foam Insulation Barrier

For several decades, this has been a highly successful method for making fire barrier coatings, where the classical formulation is a soft polymer matrix, a good char former such as a pentaerythritol or tris(2-hydroxyethyl)isocyanurate, a good charring catalyst such as ammonium polyphosphate, and a good blowing agent (spumific) to produce bubbles and to expand the molten polymer. A book, largely contributed to by French researchers, covers this approach to flame retardancy [35]. Further additives, such as talc, zeolites or TiO₂, can enhance these systems either catalytically or by forming inorganic glasses. The intumescence approach has been extensively studied for non-coating applications of thermoplastics and

can be quite effective, but has had limited commercial success largely because of the cost and hydrophilic character of the additives. An interesting self-intumescent additive, ethylenediamine phosphate, shows promise, but may not be low enough in water solubility for many polyolefin applications.

Catalysis of char formation in poorly charring polymers has been much explored but with little commercial success. In principle, a dehydrogenation or oxidative dehydrogenation catalyst should cause only the hydrogen content of a polymer to burn, with only about one-third the heat of combustion, and leaving the carbon behind to serve as a barrier. Some academic examples have been found, but no commercial application is known. This approach is theoretically attractive since there is no limit to the activity of catalysts, but the real application remains as a challenge. Possibly nano-particle catalysts would be effective.

13.9 Drip Promotion or Drip Suppression

The flow properties of molten thermoplastics during ignition or flaming can play a large part in flame retardant modes of action. At the ignition step, melting or shrinking away from the flame can prevent ignition, this being a mode by which thermoplastic textiles can pass a flame test such as NFPA 701 or the childrens' nightwear standard. Solids (such as infusible pigments or the inclusion of infusible fibers) that prevents the flow can aggravate flammability. This is discussed further in the textile chapter. The same effect may be seen in thermoplastics other than textiles.

A relatively weak flame retardancy standard such as UL 94 V2, which allows even flaming drips, can usually be passed by such systems as foamed polystyrene or non-reinforced nylons. In the case of the foamed polystyrene, inclusion of a small amount of a peroxide or other free-radical-generator which favors fragmentation, can favor the melt-flow-drip mode of extinguishment. In the case of nylons, melamine cyanurate is commonly added to favor non-flaming drip; the presence of a reinforcing solid can defeat this mode of extinguishment. On the other hand, melt flow leading to flaming drip is not allowed in some important test standards such as UL 94 V0 or V1. The most usual means to retard it is to include small (< 0.5 %) amounts of a finely-divided shear-fibrillated polytetrafluoroethylene. Finely divided silica or clay can also be used for this purpose.

13.10 Additivity, Synergism and Antagonism of Flame Retardant Combinations

Often, two or more flame retardants will act cooperatively to reach a flame retardancy goal. It is not meaningful to say that they are additive, since the relationship of flame retardant response *vs.* concentration is not often linear, so "additivity" is not clearly defined in a quantitative sense.

Sometimes the effect is much larger than would be expected from consideration of what each additive would provide if by itself, and this is usually called "synergism". It is particularly clear where one of the additives, such as antimony oxide, has practically no effect by itself but gives

a large boost to a halogen additive. Many other cases of so-called synergism are not so clear. The topic has been reviewed in detail by one of the present authors [36, 37].

Some particularly useful positive interactions ("synergism"), besides the antimony oxide-halogen case, are the following: phosphorus-containing textile finishes on cellulose, which are greatly boosted by some, but not all, nitrogen compounds; tris(chloroalkyl) phosphates in flexible polyurethane foams, greatly aided by melamine; tetrabromophthalate esters in PVC, aided by tetrachlorophthalate esters; ATH plus $\text{Mg}(\text{OH})_2$, often found better in combination in polyolefins; combinations of certain chlorocarbons such as Dechlorane Plus® with iron oxide in polyamides. Dechlorane Plus can be also synergistic with decabromodiphenyl ether in polypropylene, which is indicative of Cl-Br synergism [38]. These are discussed in the present volume in chapters on the individual polymer classes. A few demonstrable examples of phosphorus-halogen synergism have been noted but it is not general.

In many cases the reason for the beneficial combination is rather obvious, such as each component providing a different, non-competing mode of action, such as condensed phase charring together with vapor phase flame inhibition. More detail on useful combinations will be found in the chapters on each individual polymer classes.

Patentability of combinations of known ingredients requires that the combination be new, useful (beneficial) and non-obvious to "one of ordinary skill in the art." The compounder, having found a new and well-performing combination, may be able to get patent protection if it cannot be shown by the patent examiner that the "prior art" suggests such a combination, or better yet, where the prior art suggests that such a combination would be poor. It is sometimes found helpful in supporting patent prosecution arguments against obviousness, to provide comparative examples of the unsatisfactory performance of closely related compositions lying outside the range of the claimed compositions.

A few cases of antagonism in flame retardancy are known [36]. A rather important case is the combining of antimony oxide-halogen systems with phosphorus flame retardants. Some PVC formulations, even commercial ones, have such combinations. There is evidence that the antimony oxide and phosphorus may tend to at least partially counteract each other, probably due to the formation of antimony phosphate which seems to be inert as a flame retardant.

Other cases occur with thermoplastics in cases where melt flow is an important part of the flame retardant mode of action. Two notable cases are polyethylene terephthalate flame retarded by phosphorus compounds (either built in or applied by the "thermosol" treatment). As little as 0.15 % phosphorus content permits the fabric to pass the vertical flame tests. These additives or reactives work in large measure by favoring the melt drip mode of extinguishment, and are defeated by solids such as silica from silicone processing oils or pigment printing with infusible pigments, or by laminating the polyester fabric with a cellulosic fabric that acts as a wick or as a scaffold to prevent melt flow.

Glass fiber reinforcement is antagonistic to the flame retardant action of melamine cyanurate in nylon which depends on non-flaming drips. The dripping is prevented by the glass.

13.11 General Comments

The multiple modes of flame retardant action, *i. e.*, physical and chemical, condensed phase and vapor phase, are exhibited by many of the effective flame retardants in actual use. Detailed quantitative knowledge of the modes of action of each is often sparse and even contradictory. The compounder should use mode of action concepts cautiously, but they do serve to suggest effective choices and combinations. Moreover, experimental design and regression analysis using quantitative flammability measurements (as well as measurements of other properties) can be a useful tool in approaching optimum combinations [39].

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Appendix 1: Sources of Further Information on Flame Retardancy

A1.1 Books

A broad introduction to flame retardancy by one of the present authors (EDW) will be found in Weil, E. D., Flame Retardancy, *Encyclopedia of Polymer Science and Engineering*, J. Kroschwitz, Ed., John Wiley & Sons, NYC, Vol. 10, pp. 21–53 (2004). A series of articles on the main classes of flame retardants is found in the Kirk-Othmer *Encyclopedia of Chemical Technology*, John Wiley & Sons, NYC. The article on Phosphorus Flame Retardants, by one of the present authors (EDW) is in the 5th Edition, Vol. 11, 484–510 (2005).

Recent books with a range of chapters on basic and applied topics are those edited by Grand, A. F. and Wilkie, C. A., *Fire Retardancy of Polymeric Materials*, Marcel and Dekker, New York (2000). This book contains a chapter by Weil, E. D. on synergism, antagonism and additivity of flame retardants and by Levchik, S. V. and Wilkie, C. A. on polymer charring.

A book edited by Horrocks, A. R. and Price, D. *Fire Retardant Materials*, Woodhead Publishing, Cambridge, UK (2001) contains a chapter on mechanism (mode) of action of flame retardants by Lewin, M., and Weil, E. D. Second edition of this book published in 2008 contains a chapter by Levchik S. V. and Weil E. D. on progress in phosphorus flame retardants.

A thorough monograph entirely devoted to the ignition aspects of flammability, including physical, engineering and forensic aspects, has been authored by Babrauskas, V. *Ignition Handbook*, Fire Science Publishers, Issaquah, WA, 2003.

Flame chemistry (emphasizing physical chemistry) and physics is dealt with by Fristrom, R. M. *Flame Structure and Processes*, Oxford University Press, Oxford, UK (1995). An earlier but very broad coverage of the physics and chemistry of the combustion of polymers is given in the monograph by Cullis, C. F. and Hirschler, M. M. *The Combustion of Organic Polymers*, Clarendon Press, Oxford, UK (1981). (1990). A treatise on principles of combustion by Kuo, K. K. *Principles of Combustion*, 2nd Edition, Wiley, New York (2005) presents a more detailed and rigorous mathematical treatment, as does a treatise on combustion by Annamalai, K. and Puri, I. K. *Combustion Science and Engineering*, CRC Press, Boca Raton, FL (2007)

A good summary of fire hazards, materials specifications and standards as well as flame retardant materials used in building and transportation in the book edited by Harper, C. A. *Handbook of Building Materials for Fire Protection*, McGraw-Hill, New York, (2004).

Compendium of world-wide test methods was edited by Troitzsch, J., *Plastics Flammability Handbook*, 3rd Edition, Hanser Publishers, Munich/Hanser-Gardner, New York, 2004.

A1.2 Conferences

The American Chemical Society sponsored conferences on Fire and Polymers, covering the entire field with both basic and applied papers, in 1989, 1994, 1999, 2004 and 2008. These all are available in symposium volumes edited by Nelson G.L. and Wilkie C.A., *Fire and Polymers*, American Chemical Society Symposium Series 425, 599, 797 and 922 respectively, Washington, DC. The volume from the 2008 conference is in publication.

An International Conference on Recent Advances in Flame Retardancy of Polymeric Materials has been held annually. A series of annual conferences is held, starting in 1990, and continuing into 2009 covering both basic and applied topics, under auspices of the Business Communications Co.. The papers have been made available in bound volumes. Citations from many of these papers are given in our present book.

Basic and applied papers are available from a meeting (held every two years) in London cosponsored by British Plastics Federation (6 Bath Place, Rivington St., London EC2A 3JE, England). Separate volumes *Flame Retardants* '90, '92, '94 etc. were published by Elsevier Applied Science, London and later Interscience Communications, Greenwich, UK.

A polymer additives conference, encompassing flame retardants, has been held annually (last in 2006) in the U.S.A. under auspices of Executive Conference Management Co. Selected papers from early conferences (1997–2000) were published in two volumes edited by Al-Malaika, S., Golovoy, A. and Wilkie, C.A. *Chemistry and Technology of Polymer Additives* (1999) and *Specialty Polymer Additives* (2001), Blackwell Science, Oxford, UK.

The Fire and Materials Conference, lately held in San Francisco, emphasizes regulatory, testing, design and material science aspects. Proceedings are available from Interscience Communications, 24 Quentin Road, London SE13 5DF, UK, Intercomm@dia1.pipex.com.

A European Meeting on Fire Retardancy and Protection of Materials (European Conference on Fire Retardant Polymers) is held biannually. This emphasizes the materials, testing, environmental and regulatory aspects especially from an EU perspective. Proceedings of this conference were published either as special issues of *Polymer Degradation and Stabilization*, *Macromolecular Chemistry*, or *Polymer International* or as separate volumes. These volumes are:

1. *Fire Retardancy of Polymers. The Use of Intumescence*, Le Bras, M., Camino, G., Bourbigot, S., and Delobel, R., (Eds.), The Royal Chemical Society, Cambridge, 1998
2. *Fire Retardancy of Polymers. New Applications of Mineral Fillers*, Le Bras, M., Wilkie, C.A., Bourbigot, S., Duquesne, S. and Jama, C., The Royal Chemical Society, Cambridge, 2005
3. *Advances in the Flame Retardancy of Polymeric Materials. Current Perspectives Presented at FRPM '05*, Scharrel, B., (Ed.), Books on Demand GmbH, Norderstedt, Germany, 2007

A1.3 Journals and Business Periodicals

Recommended periodicals are *Journal of Fire Sciences*, bimonthly, published by Sage Publications, 1 Oliver's Yard, 55 City Road, London EC1Y 1SP, UK. 44-(0)20 7324 8500.

subscriptions@sagepub.co.uk <http://www.sagepublications.com>., a leading American journal in this field. Also, *Fire and Materials*, bimonthly, published by John Wiley & Sons Ltd., Baffins Lane, Chichester, Sussex P019 IUD, UK., a leading European journal in this field.

A world-wide coverage of all chemistry-related aspects of flame retardancy, including patents, is provided by biweekly Chemical Abstracts as a specialized selection called *CA Selects — Flammability*, Chemical Abstracts Service, P.O. Box 3012, Columbus, Ohio 43210. Inexpensive subscription is available for ACS members. This is probably the best single source for complete surveillance of the field. It includes Japanese, Chinese and Korean patents and non-patent sources, which are increasingly important but difficult or costly to monitor.

The *Fire Safety & Technology Bulletin*, published by Hirschler, M. and Grayson, S.J., GBH International, 2 Friar's Lane, Mill Valley, CA 94941 (415/388-8278), provides monthly coverage of technical, business and regulatory developments, including insight into pending and recent regulations and non-governmental standards, recent and pending committee deliberations, business news including press releases on new products, abstracts of recently published U.S. patent applications, and a schedule of forthcoming technical, regulatory and standards-setting meetings.

Flame retardancy topics often appear in:

1. *Polymer Degradation and Stability*
2. *Journal of Applied Polymer Science*
3. *Combustion and Flame*
4. *Journal of Cellular Plastics*
5. *Polymer Composites*
6. *Journal of Vinyl and Additive Technology*
7. *European Polymer Journal*
8. *Polymers for Advanced Technologies**
9. *Polymer International*
10. *Polymer Engineering and Science*
11. *Plastics Additives and Compounding*
12. *Fire Safety Journal*
13. *Wire Technology International*
14. *Printed Circuit Fabrication*
15. *International Journal of Polymeric Materials*
16. *Plastics Engineering*
17. *Modern Plastics*
18. *Rubber Chemistry and Technology*
19. *Journal of Coated Fabrics*
20. *Textile Chemist and Colorist*
21. *Kunststoffe International* (translation of German Plastics journal)
22. *GAK* (*Gummi, Fasern, Kunststoffe*)

The German publications generally carry articles in English as well as German.

* *Polymers for Advanced Technologies* Vol. 19, Issue No. 6, pp. 443–723, June 2008 is a special issue consisting entirely of articles on flame retardancy in celebration of the 90th birthday of Prof. Menachem Lewin, a pioneer researcher in this field. It can be ordered from www.interscience.wiley.com/journal/pat

A1.4 Reviews by the Present Authors with More-Inclusive Coverage

The authors of this book also have composed a series of reviews of inclusive type, dealing with academic studies, including theory and mechanisms, discontinued or at least not-yet-commercialized industrial studies, unexploited patents, and other sources which did not fit the main theme of the present book and the *Journal of Fire Sciences* reviews. Those which have been published to date are:

1. **Combustion and Fire Retardancy of Aliphatic Nylons**,
Polymer International (2000) 49, pp. 1033–1073.
2. **A Review on Thermal Decomposition and Combustion of Thermoplastic Polyesters**,
Polymers for Advanced Technologies (2004), 15, pp. 691–700.
3. **Thermal Decomposition, Combustion and Flame-Retardancy of Epoxy Resins — A Review of the Recent Literature**, *Polymer International* (2004), 53, pp. 1901–1929.
4. **Thermal Decomposition, Combustion and Fire-Retardancy of Polyurethanes — A Review of The Recent Literature**, *Polymer International* (2004), 53, pp. 1585–1610.
5. **Overview of Recent Developments in the Flame Retardancy of Polycarbonates**,
Polymer International (2005), 54, pp. 981–998.
6. **Flame Retardancy of Thermoplastic Polyesters — A Review of the Recent Literature**,
Polymer International (2005) 54, pp. 11–35.
7. **Overview of the Recent Literature on Flame Retardancy and Smoke Suppression in PVC**, *Polymers for Advanced Technologies* (2005) 16, pp. 707–716.
8. **A Review of Recent Progress in Phosphorus-based Flame Retardants**,
Journal of Fire Sciences (2006) 24, pp. 345–364.
9. **New Developments in Flame Retardancy of Styrene Thermoplastics and Foams**,
Polymer International (2008) 57, pp. 431–448.

A1.5 Internet Information Sources

1. A portal to NIST's fire related publications and projects: <http://www.fire.nist.gov>
2. A bibliographic database on flame retardants assembled by NIST:
<http://fire.nist.gov/bfrpubs/fireall/key/key628.html>.
3. Reviews and links on various topics including flame retardants. Product information from U. S. Borax, Ciba, ICL-IP, Atofina. <http://www.specialchem.com>

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4. Product information on additives including flame retardants, from Albemarle, Supresta/ICL-IP, Cytec, GE and others. On-line source for samples. <http://www.polymeradditives.com>
 5. <http://www.cefic-efra.com> for information about the European Flame Retardants Association.
 6. <http://www.ebfrip.org> European Brominated Flame Retardant Industry Panel, a trade organization which defends the continued safe use of these products.
 7. <http://www.iaoia.org> International Antimony Oxide Industry Association, which provides current information on risk assessments and regulatory activity dealing with antimony oxides.
 8. <http://www.techstreet.com/intertekgate.tmpl> The Intertek Standards Store, a source for standards including ASTM, IEEE, EN, UL, ASME, DIN, NFPA.

Appendix 2: Directory of Flame Retardant Manufacturers, Distributors, and Compounders

Name	Location	Phone	Web	Products
Addcomp Holland bv	Nijverdal, Netherlands	+31-548-620403	www.addcomp.nl	F.r. masterbatches
AddMaster Ltd., UK	Stafford, UK	+44-1785-225656	www.addmaster.co.uk	F.r. masterbatches
Akzo Nobel Polymer Chemicals bv	Amersfoort, Netherlands; Chicago	+31-33-467-6767; 1-312-544-7012	www.akzonobel-polymerchemicals.com	Perkalite® organoclay
Albemarle Corp. USA	Baton Rouge, LA	1-800-535-3030	www.albemarle.com	Bromine compounds, magnesium hydroxide, organic phosphates
Albemarle Corp. Europe	Louvain-la-Neuve, Belgium	+32-10-48-1711		
Allied Color and Additives Pty Ltd.	Victoria, Australia	+61-3-9873-4255	www.alliedcolor.com.au	
Almatis, formerly Alcoa	Bauxite, AR	1-800-860-3290	www.almatis.com/alumina/default.asp	Alumina trihydrate
Ameribrom Inc., (DSBG) (see ICL-IP)				
American Industries Supply S.A. de C.V.	Garza Garcia, Mexico	+52-81-8336-6130	www.aissa.biz	F.r. additives and masterbatches
Americhem, Inc.	Cuyahoga Falls, OH	+1-800-228-3476	www.americhem.com	Plastic and synthetic fiber concentrates including flame retardants

Name	Location	Phone	Web	Products
Amfine Inc. (sales outlet for Asahi Denka)	Upper Saddle River, NJ	+1-201- 818-0035	www.amfine.com	Aryl diphosphates, intumescent phos- phate salt
Ampacet Co.	Tarrytown, NY	+1-914- 631-6600	www.ampacet.com	F.r. masterbatches
Apexical Inc.	Spartanburg, SC	+1-800- 552-7399	www.apexical.com	Textile flame retar- dants
Argus Additive Plastics GmbH	Bueren, Germany	+49-2951- 99090	www.argus-additive. com	F.r. additives and masterbatches
Asbury Carbons	Asbury, NJ	+1-908- 537-2155	www.asbury.com	Expandable graphite
Astaris LLC	St. Louis, MO	+1-314- 983-7500	www.astaris.com	Ammonium polyphosphates
BASF Corp., N.A. Hq.	Florham Park, NJ	+1-973- 245-6000	www.basf.com	F. r. melamine foam and fiber
Bedford Specialty Sales, Inc. (distribu- tor.)	Shirley, MA	+1-800- 815-7429	www.befordsales.com	Antimony oxide, brominated f.r.
Brenntag North America	Reading, PA	+1-610- 926-6100	www. brenntagnorthamerica. com	Zinc borate, magne- sium hydroxide, other flame retar- dants
Bold Vision Sdn. Bhd.	Port Klang, Malaysia	+603-3165- 8288	www.boldvision.com. my	F.r. masterbatches
Broadview Technolo- gies, Inc.	Newark, NJ	+1-973- 465-0077	www.broadview-tech. com	Melamine pyrophosphate, ethylenediamine phosphate, intumes- cent mixtures
Buckman Laborato- ries, Inc.	Memphis, TN	+1-800- 282-5626	www.buckman.com	Barium metaborate, other borates

Name	Location	Phone	Web	Products
Canada Colors and Chemicals Ltd. (distributor)	Mississauga, Ontario	+1-905-454-6900	www.canadacolors.com	Alumina trihydrate, antimony oxide, organic phosphates, brominated f.r.
CCC Plastics	Colborne, Ontario, Canada	+1-905-355-2537	www.cccplastics.com	F.r. masterbatches
Chemische Fabrik Budenheim	Budenheim, Germany	+49-6139-89-224	www.budenheim-cfb.com	Ammonium polyphosphate, melamine phosphate, organic phosphates
Chang Chun Plastics Co., Ltd	Taipei, Taiwan	+886-2-2503-8131	www.ccp.com.tw	Organic phosphates, brominated epoxy oligomers
Chemisphere Ltd.	Chester, UK	+44-1244-320878	www.chemisphere.co.uk	Antimony trioxide, antimony pentoxide
Chemtura (formerly Great Lakes Chemical and Crompton)	W. Lafayette, IN	+1-800-428-7947	www.chemtura.com	Bromine compounds, organic phosphates, antimony oxide, smoke suppressants
Chenguang Research Institute of Chemical Industry	Chengdu, China	+86-28-855-12532	www.cggs-chem.com	Red phosphorus masterbatches, melamine cyanurate
Ciba Plastics Additives Group (acquired by BASF)	Basel, Switzerland Tarrytown, NY	+41-61-63-61111 +1-800-431-2360	www.cibasc.com	Melamine phosphates, melamine cyanurate, NOR 116
Clariant GmbH	Sulzbach, Germany; Charlotte, NC	+49-4102-487-127 +1-800-411-7113	www.clariant.com	Red phosphorus, ammonium polyphosphate, phosphinate salts, organic phosphates
Clariant Masterbatch	Ahrensburg, Germany; Winchester, VA	+49-4102-487-124 +1-540-665-1865	www.clariant.masterbatches.com	F.r. masterbatches

Name	Location	Phone	Web	Products
Cromex S/A	Sao Paulo, Brazil	+55-11-3856-1000	www.cromex.com.br	F.r. masterbatches
Cytec Industries	West Paterson, NJ	+1-800-652-6013	www.cytec.com	Melamine phosphates, melamine, melamine resins, THPS
Daihachi Chemical Industry Co.,	Chuo-ku, Osaka, Japan	+81-6-6201-1455	www.daihachi-chem.co.jp	Organic phosphates, phosphonates, chloroalkyl phosphates
Dai-ichi Kogyo Seiyaku Co., Ltd	Tokyo, Japan	+81-3-546-35171	www.dks-web.co.jp	Brominated f.r.
Dover Chemical Co.	Dover, OH	+1-800-321-8805	www.doverchem.com	Chloro- and chlorobromoparaffins, f.r. rotational molding compounds
Dow Chemical Co., Coatings & Resins Dept.	Midland, MI	+1-800-441-4369	www.dow.com	Bromoepoxies, PVDC latices
Dow Corning Co.	Midland, MI	+1-800-248-2481	www.dowcorning.com	Silicone-based synergists
Durr Marketing Associates (distributor)	Pittsburgh, PA	+1-800-937-3877	www.durrmarketing.com	Alumina trihydrate, antimony oxide, borates, organic phosphates, brominated f.r., magnesium hydroxide, melamine salts
Dynamic Modifiers LLC	Atlanta, GA	+1-404-349-0900	www.dynamicmodifiers.com	F.r. masterbatches
Eastman Chemical Products	Kingsport, TN	+1-800-251-0351	www.eastman.com	Triethyl phosphate
Emerald Performance Materials	Charlotte, NC	+1-800-545-1067	www.emeraldmaterials.com	Textile flame retardants, particularly backcoating

Name	Location	Phone	Web	Products
EMSA Chemicals	Barcelona, Spain	+34-93-589-1242	www.emsachemicals.com	Nondusting anti-mony trioxide
Emsar Polymers Ltd.	Staffordshire, UK	+44-1782-563258	www.emsarpolymers.co.uk	F.r. masterbatches
E-Z Color Co.	Fremont, OH	+1-419-332-8000	www.e-zcolor.com	F.r. masterbatches
Ferro Corp.	Cleveland, OH	+1-800-321-9942	www.ferro.com	Bromine and chlorine compounds; alkyl diphenyl phosphates
Flame Chk, Inc. (representing Chemische Fabrik Budenheim, Germany and Budenheim Iberica, Spain)	Medford, NJ	+1-609-953-0456	www.flamechk.com	Ammonium polyphosphates, melamine phosphates, intumescent phosphates
GE Plastics (see Sabic Innovative Plastics)				
Graftech, Inc.	Cleveland, OH	+1-800-253-8003	www.graftech.com	Expandable graphite
Great Lakes Chemical Co., (see Chemtura)				
Harwick Standard Distribution Co.	Akron, OH	+1-330-798-9300		Antimony oxide, borates, chloroparaffins, organic phosphates
Heroflon Srl.	Collebeato, Italy Roselle Park, NJ	+39-030-251-0211 +1-908-241-7355	www.heroflon.com	Free-flowing PTFE

Name	Location	Phone	Web	Products
Huber Engineered Minerals	Atlanta, GA	+1-866-564-8237	www.huber.com	Alumina trihydrate, magnesium hydroxide
Israel Chemical Ltd. — Industrial Products (former Dead Sea Bromine) ICL-IP, America (former Ameribrom and Supresta)	Beer-Sheva, Israel St. Louis, MO	+972-8-629-7608 +1-877-661-4272 +1-800-666-1200	fr.ameribrom@icl-ip.com	Bromine compounds, magnesium hydroxide, melamine cyanurate, aryl phosphates, chloroalkyl phosphates, urethane foam additives and reactives
Italmatch Chemicals Srl.	Genova, Italy	+39-010-642810	www.italmatch.it	Red phosphorus, melamine cyanurate, phosphorus f.r.
Jiangsu Yoke Technology Co., Ltd.	Yixing City, China	+86-510-871-26518	www.yokechem.com	Organic phosphates and chlorophosphates
JLS Chemical Inc. Overseas Sales & Marketing	City of Industry, CA	+1-626-968-3608	www.jlschemicalusa.com	Ammonium polyphosphate, melamine cyanurate, N-P intumescent, Br-N additive, Cl-Br containing diphosphate
Kafrit Industries Ltd.	Kfar Aza, Israel	+972-8-680-9845	www.kafrit.com	F.r. masterbatches
Kyowa Chemical Industry Co.	Kagawa, Japan	+81-87-841-9156	www.kyowa-chem.co.jp	Alumina trihydrate, magnesium hydroxide
Laizhou Changhe Chemical Co., Ltd	Laizhou, China	+86-535-228-7639	www.lzchanghe.com	Alumina trihydrate, magnesium hydroxide

Name	Location	Phone	Web	Products
Lanxess Corp. (formerly part of Bayer)	Cologne, Germany Pittsburgh, PA	+49-221-16470 +1-412-890-3546	www.lanxess.com	Organic phosphates, phosphonates, f.r. grades of PBT, PET, nylons
Luzenac (see Rio Tinto Minerals)				
3M Co.	St. Paul, MN	+1-800-364-3577	www.3M.com	Fire barrier materials, polyfluoroalkylsulfonate salts
MAL Hungarian	Budapest, Hungary	+36-1-309-4200	www.mal.hu	Aluminum trihydrate
Marshall Additive Technologies	Southfield, MI	+1-248-353-4100	www.rjmarshall.com	Alumina trihydrate, magnesium hydroxide, zinc stannate, zinc hydroxystannate, ammonium octamolybdate, zinc borates, mixed-metal flame and smoke suppressants
Martin Marietta Magnesia Specialties, Inc.	Baltimore, MD	1-800-648-7400	www.magspecialties.com	Magnesium hydroxide
Membrana GmbH	Orenburg, Germany	+49-6022-813200	www.membrana.com	Acurel® solid concentrates of liquid flame retardants.
Minelco Minerals	North Lincolnshire, UK	+44-1724-277411	www.minelco.com	Alumina trihydrate, magnesium hydroxide, Ultracarb
MJL Industrial Inc.	Hockessin, DE	+1-302-234-0898	www.mjlindustrial.com	Trader of brominated, phosphorus and inorganic f.r.
Modern Dispersions Inc.	Leominster, MA	+1-978-534-3370	www.moderndispersions.com	F.r. masterbatches

Name	Location	Phone	Web	Products
Nabaltec GmbH	Schwandorf, Germany	+49-9431-53-464	www.nabaltec.de	Alumina trihydrate, boehmite, magnesium hydroxide
Noveon Textile Specialties (see Emerald Performance Materials)				
Nyacol Nano Technologies, Inc.	Ashland, MA	+1-508-881-2220	www.nyacol.com	Antimony pentoxide, nanoparticle antimony oxides, sodium antimonate
Omya UK Ltd.	Derby, UK	+44-1332-674000	www.omya.co.uk	Trader of alumina trihydrate, magnesium hydroxide, antimony trioxide, brominated f.r., zinc borate
Otsuka Pharmaceutical Co., Ltd	Tokyo, Japan	+81-3-6717-1400	www.otsuka.com	Phosphazenes
Overbeck & Co. GmbH	Oyten, Germany	+49-4207-91125	www.overbeck-bremen.de	F.r. masterbatches
OxyChem (Occidental Chem.)/Laurel Industries	Niagara Falls, NY	1-800-233-1022	www.oxychem.com	Dechlorane® Plus
Palmer Holland Inc.	North Olmsted, Ohio	1-800-635-4822	www.palmerholland.com	Distributor of wide range of flame retardants
Phoenix Plastics Co.	Conroe, TX	+1-936-760-2311	www.phoenixplastics.com	F.r. masterbatches
PolyChem Alloy Inc.	Lenoir, NC	1-877-722-2638	www.polychemalloy.com	F.r. masterbatches

Name	Location	Phone	Web	Products
Polymer Additives Group	Indianapolis, IN	+1-317-290-5006	www.pagholdings.com	ATH, magnesium hydroxide, various mixed metal oxide, PVC smoke and flame suppressants
Polymer Dynamix	Rahway, NJ	+1-732-381-1600	www.polymerdynamix.com	F.r. masterbatches
Polymer Products Co.	Stockertown, PA	+1-800-836-8589	www.polymerproductscompany.com	Flame retardant compounds and concentrates
PolyOne Corp.	Avon Lake, OH	+1-866-765-9663	www.polyone.com	Flame retardant compounds, concentrates, including "nanoclay" masterbatches
Polytechs	Cany Barville, France	+33-2-3557-8181	www.polytechs.fr	F.r. masterbatches
Produits Chimiques de Lucette	Le Genest Saint Isle, France	+33-2-4301-2310	www.pcdlucette.com	Antimony trioxide
Rajiv Plastic Industries	Mumbai, India; Garden City Park, NY	+91-22-669-29701 +1-516-850-9635	www.rajivplastics.com	F.r. masterbatches
Rejenmor Inc.	Burlington, Ontario	+905-681-7532	www.rejenmor.com	Wide range of Br, Cl, P based f.r., antimony oxide, alumina trihydrate, magnesium hydroxide, zinc borate, smoke suppressants
Rhodia (acquired Albright & Wilson f.r. products)	Hertfordshire, UK; Glen Allen, VA	+44-19-2348-5868; +1-843-740-5211	www.rhodia.com	Phosphonates, phosphonium compounds: textile flame retardants
Rio Tinto Minerals	Denver, CO	+1-303-643-0400	www.riotintominerals.com	Zinc borate, formerly U.S. Borax products; talcs, formerly Luzenac products

Name	Location	Phone	Web	Products
H. M. Royal Co. (distributor)	Trenton, NJ	+1-609-396-9176	www.hmroyal.com	Alumina trihydrate, antimony oxide, borates, phosphates, chloroparaffins, brominated f.r.
RTP Co.	Winona, MN	1-800-433-4787	www.rtpcompany.com	Flame retardant polyolefin, polyamide and engineering resin compounds
Sabic Innovative Plastics (former GE)	Pittsfield, MA	+1-413-448-5800	www.geplastics.com	F.r. grades of PBT, ABS, PC, ABS-PC, PPE, PPO-HIPS, polyimides
Samhwa Co.	Seoul, Korea	+82-2-2671-0477	www.sam-chem.com	F.r. masterbatches
Sanko Chemical Industry Co., Ltd.	Otake-shi, Japan	+81-827-52-3111	www.sanko-kagaku.co.jp	DOPO, HCA-DOPO
A. Schulman Co.	Akron, OH	1-800-547-3746	www.aschulman.com	Masterbatches including flame retardant compounds
Sherwin Williams Co.	Cleveland, OH	+1-216-566-1294	www.sherwin-williams.com	Smoke-suppressant molybdenum and zinc compounds
SICA	Chauny, France	+33-323-403530	www.sica-chauny.com	Antimony trioxide
Sinochem Jiangsu Co.	Nanjing, China	+86-25-868-90810	www.sinochemjiangsu.com	Alumina trihydrate, magnesium hydroxide, organic phosphates and chlorophosphates, brominated f.r.
Sloss Industries Chemical Division	Birmingham, AL	+1-205-808-7915	www.sloss.com	Potassium sulfonate flame retardants for polycarbonates
Special Materials Co.	Cherry Hill, NJ	+1-609-720-0080 +1-646-366-0400		Imports from China of flame retardant finishes for cotton and polyester

Name	Location	Phone	Web	Products
Struktol	Stow, OH	+1-330-928-5188	www.struktol.com	DOPO, phosphorylated epoxy
Sukano Products	Schindellegi, Switzerland	+41-44-787-5777	www.sukano.com	F.r. masterbatches
Supresta US LLC (see Israel Chemicals Ltd. — Industrial Products; ICL-IP),				
Techmer PM	Rancho Dominguez, CA	+1-310-632-9211	www.techmerpm.com	Non-halogen f.r. additive for wire and cable, f.r. masterbatches
Teknor Color Co.	Pawtucket, RI	+1-401-725-8000	www.teknorcolor.com	F.r. masterbatches
3N International Inc., (importer from China)	Akron, OH	1-330-665-3821	www.3ninc.com	ammonium polyphosphate, antimony oxide, alumina trihydrate, borate, stannates, organic phosphate, brominated f.r.
Tipco Industries	Mumbai, India	+91-22-2883-5251	www.tipco-india.com	F.r. masterbatches
Tosaf Compounds	Afula, Israel	+972-4-642-0419	www.tosaf.com	F.r. masterbatches
TP Composites Inc.	Aston, PA	+1-610-358-9001	www.tpcomposites.com	F.r. composites and masterbatches
Univar Co. (distributor)	Redmond, WA	425-638-4900	www.univar.com	alumina trihydrate, antimony oxide, brominated f.r., borates, organic phosphates
VIBA S.p.A.	Tradate, Italy	+39-0331-812591	www.vibagroup.com	F.r. masterbatches
3-V Inc. (importer)	Weehawken, NJ	+1-800-441-5156	www.3V.com	Melamine cyanurate

Name	Location	Phone	Web	Products
U.S. Borax and Chemical Corp. (see Rio Tinto Minerals)				
Unitex Chemical Corp.	Greenville, NC	+1-336-378-0965	www.unitexchemical.com	Phosphates, bromines, smoke suppressants
Velsicol Co.	Rosemont, IL	+1-800-843-7759	www.velsicol.com	Chlorendic anhydride
Weidong International Group Ltd.	Weifang, China	+86-536-888-1111		Brominated f.r.
Wells Plastics Ltd.	Stone, UK	+44-1785-817-421	www.wellsplastics.com	F.r. masterbatches
Xmold Polymers Pvt Ltd.	Chennai, India	+91-44-261-84401	www.xmoldpolymers.com	F.r. masterbatches

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